Helium nanodroplet assisted synthesis of bimetallic Ag@Au nanoparticles with tunable localized surface plasmon resonance

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Abstract. Nanoparticles with tunable localized surface plasmon resonance have been prepared by synthesis in helium nanodroplets. Subsequent surface deposition allows for the formation of substrates which can be employed for surface-enhanced Raman spectroscopy (SERS). The assembly of Ag@Au core@shell clusters of about 5 nm diameter in helium droplets with different Ag: Au ratio allows to tune the surface plasmon resonance between the plain Ag resonance at 447 nm and the Au resonance at 555 nm. For the fabricated substrates only a single plasmon resonance is observed in the UV/vis absorption spectra. The prepared nanostructures have been functionalized with 4-methylbenzenethiol (4-MBT) molecules and SERS spectra have been recorded. The results demonstrate the potential of the helium droplet synthesis approach, opening up a new route to the formation of tailored plasmonic nanoparticles and functional nanostructures.

1 Introduction

Nano-sized particles have paved the way for exciting new research and applications in science and technology. Today, nanoparticles are ubiquitous and have found application in catalysis \cite{1} and photovoltaics \cite{2} as well as in chemistry \cite{3}, biology \cite{4} and medicine \cite{5}. Hybrid nanoparticles, in particular, play an important role in emerging applications as they allow to tailor particle characteristics by deliberately combining materials with desired magnetic, optical or chemical properties \cite{6}. The great potential of such nanoparticles and nanostructures assembled thereof is calling for novel synthesis methods capable to rapidly explore a large variety of different material combinations. Here, we introduce the helium nanodroplet synthesis method as a novel approach for the production of functional hybrid nanoparticles with tailored plasmonic properties.

The advantages that come with the helium droplet approach are the (i) intrinsic inertness of the synthesis environment (liquid helium) that does not involve any solvents, surfactants or other chemicals, (ii) the large variety of dopants that can be combined and (iii) the cold environment (0.37 K) \cite{7,8} that enables the production of nanoparticles with a core@shell configuration independent of the thermodynamically favored structure \cite{9}. In the present study, we chose the Ag@Au system in order to demonstrate the controlled formation of plasmonic nanoparticles and nanostructures by helium droplet synthesis. However, in general the approach allows to select nanoparticle constituents from a large variety of materials.

Many of the outstanding optical properties of plasmonic materials are related to surface plasmon resonances or, in the case of coinage metal nanoparticles smaller than the wavelengths of visible light, localized surface plasmon resonances (LSPR). These plasmons can be understood as collective oscillations of electrons within the nanoparticle. The spectral position of a LSPR thereby depends strongly on the structure, shape and size of the particle \cite{6}. The resonant interaction between an electromagnetic field and the surface plasmon causes a concentration of electromagnetic radiation close by the nanoparticle surface, an effect which forms the foundation of surface-enhanced Raman scattering (SERS): when a Raman active molecule is attached to the surface of a metal nanoparticle and exposed to electromagnetic radiation resonant with the LSPR it experiences a strongly enhanced field, which can boost the Raman signal by orders of magnitude \cite{4}.

Typically, Au or Ag nanostructures are used as SERS substrates, however, hybrid nanoparticles pose very promising building blocks for the preparation of novel SERS substrates for emerging and future applications \cite{6,10}. A well characterized material combination in this context is represented by Ag–Au hybrid nanoparticles \cite{11}, which we chose to demonstrate the capabilities of our
2.1 Nanoparticle synthesis

The employed helium droplet apparatus has been described in reference [29]. Bimetallic nanoparticles are formed by guiding a helium droplet beam through two independent pickup zones at which enclosed, heated crucibles establish an increased vapor pressure of the desired dopant material. The subsequent arrangement of two of such pickup cells allows for the doping with two different materials. Under such conditions core@shell nanoparticles can be formed, where the material introduced first forms the core and the second the shell [20,21]. Subsequently, the particles can be deposited on any desired substrate, thereby the surrounding helium acts as a cushion that is stripped off upon impact, dissipating the released energy and resulting in a very soft deposition [22,23].

In the recent years helium droplets have evolved from a pure spectroscopic matrix [7,8] to a synthesis method for nanoparticles [24–28]. However, the vast majority of works dealing with nanoparticle synthesis is focused on the investigation of particle size, structure and morphology. Here, we expand the helium droplet synthesis approach into the field of plasmonics by presenting a new tool for the production of bimetallic plasmonic nanoparticles and nanostructures.

2.2 UV/vis absorption spectroscopy

UV/vis absorption spectra were recorded employing a Shimadzu UV-1800 spectrophotometer. The nanoparticles were deposited by introducing a fused silica microscope slide (Corning 7980, fused silica, 1 mm thickness) into the beam. The slide is subsequently taken out of the vacuum and placed into the spectrophotometer to acquire the spectra shown in Figure 4, using a second fused silica slide as reference.

2.3 Transmission electron microscopy (TEM)

For TEM experiments the clusters are deposited on TEM grids (Ted Pella, Inc., Prod. No. 01824), covered with an amorphous carbon film with a thickness of 3 nm. The TEM images shown in Figure 1 are recorded with a 120 kV LaB6 FEI Tecnai 12 transmission electron microscope, equipped with a Bio Scan Camera (Gatan, Model 792). High-resolution scanning transmission electron microscopy (HR-STEM) is performed using a probe-corrected FEI Titan3 G2 60-300 instrument. The STEM images shown in Figure 3 have been acquired using a high-angle annular dark-field (HAADF) imaging detector. Note that during transport from the helium droplet apparatus to the TEM instrument the samples are exposed to air for a short period of time, which should have no effect on the deposited Ag and Au materials.

2.4 Raman spectroscopy

After recording the absorption spectra of nanoparticles deposited on the fused silica glass slides, the substrates were functionalized with 4-methylbenzenethiol (4-MBT) molecules. The functionalization is done by immersing the
substrate in a 0.1 mM solution of 4-MBT in DI water for 1 h. Excess 4-MBT is removed by subsequent immersion in ethanol. Raman spectra were acquired employing a LabRam HR 800 spectrometer. The used laser wavelengths (and powers) are 473 nm (12.5 mW), 532 nm (12.5 mW) and 633 nm (15 mW). A x10 Olympus MplanN (N.A. 0.25) objective was used to focus the laser onto the sample. For every substrate 64 spectra were measured across an area of $500 \times 500 \mu m$ with an acquisition time of 8 s (and 2 accumulations) per spectra. The shown Raman spectra in Figures 5 and 6 correspond to the average of these 64 spectra. Enhancement factors $EF$ were determined according to the definition and procedure provided by Le Ru et al. [33]:

$$EF = \frac{I_{SERS} N_{Ref}}{I_{Ref} N_{SERS}} = \frac{I_{SERS} c_{Ref} H_{eff}}{I_{Ref} A_{\mu_S}}. \tag{1}$$

All band intensities ($I_{SERS}$, $I_{Ref}$) were determined using the peak fit routine of the LabSpec 6 software. Reference measurements were done for two different solutions (ethanol and isopropanol; molar concentration $c_{Ref} = 0.5 M$) in order to obtain reference intensities for all bands without interference from the solvent. The effective height of the scattering volume $H_{eff} = 174 \mu m$ was determined as described in the supplementary information of Le Ru et al. [33] The surface density $\mu_S$ of 4-MBT is taken from Camargo et al. [34] ($\mu_S = 5.3 \text{ nm}^{-2}$). From the TEM images, which show a projection of the deposited nanoparticles, the ratio of the surface area of the metallic nanoparticles to the total substrate area is estimated as $A = 0.58$ by assuming spherical particles.

### Table 1. Summary of the determined surface coverage (sc) per hour and the mean particle diameter $d$ estimated by assuming spherical particles for nanoparticles with Ag:Au ratios of 2:1, 1:1 and 1:2, obtained from the recorded TEM images. In addition, the full width at half maximum (FWHM) of the particle size distribution for each Ag:Au ratio, shown in Figure 2, is listed.

| Ag:Au ratio | sc per hour  | $d$ (nm) | FWHM |
|-------------|--------------|----------|-------|
| 2:1         | (4.7 ± 0.6)% | 4.7      | 2.0   |
| 1:1         | (3.6 ± 0.2)% | 6.5      | 4.9   |
| 1:2         | (4.7 ± 0.4)% | 4.4      | 2.2   |

#### 3 Results and discussion

Figure 1 shows a survey of bright-field (BF) images of the prepared bimetallic Ag@Au core@shell particles with Ag:Au ratios adjusted to 2:1 (red frame, a), 1:1 (green frame, b) and 1:2 (blue frame, c), recorded by transmission electron microscopy (TEM). Note that the ratio refers to the estimated ratio of the number of atoms, which can be easily controlled by adjusting the temperatures of the pickup-ovens [31]. The nanoparticles were deposited on standard amorphous carbon TEM grids immediately after deposition on fused silica substrates at the same helium droplet source conditions in order to reveal insight into the surface coverage, particle size and structure. The intensity in the shown BF images depends on the atomic number ($Z$), i.e. bright areas correspond to Ag rich zones whereas dark regions indicate Au rich zones. Note that only image (b) has been obtained upon deposition for four hours, similar to the samples used in the optical experiments. Nanoparticles in images (a) and (c) have been deposited for 30 min on the TEM grids. The comparison of particles prepared with different deposition times reveals insight into coagulation processes that can proceed upon deposition: while for low surface coverage nearly all particles remain separated, upon 4 h of continuous deposition the surface coverage is high enough that a fraction of the particles coagulates and forms larger structures.

The obtained surface coverages (sc) and mean particle diameters $d$ (estimated by assuming spherical particles) are listed in Table 1. Note that in order to ease...
a comparison, the surface coverages have been scaled to one hour of deposition, neglecting the statistic nature of the process, i.e. particles may be deposited on top of each other. It can be seen that coagulation, which becomes relevant in case of the longer deposition time for the 1:1 ratio particles, manifests in an increase of the estimated mean particle diameter and, to some extent, also in a decrease of the surface coverage.

The particle size distributions are shown in Figure 2, the corresponding full width at half maximum (FWHM) of each distribution is listed in Table 1. Here, the effect of particle coagulation becomes obvious by comparing the distributions in panels (a) and (c), where particles have been deposited for 30 min, to the distribution in panel (b) for which the particles have been deposited for 4 h. Coagulation leads to a significant broadening of the distribution towards larger particle sizes. We note that the coagulation process may differ between the amorphous carbon TEM grid substrate and the fused silica glass slides. However, it has to be considered in the interpretation of the UV/vis absorption spectra that a fraction of larger particles, which may not retain a core@shell structure, can contribute to the signal.

While the images in Figure 1 allow a characterization of the particle sizes and surface coverages, the resolution is too low in order to reveal insight into structural details, in particular, the core@shell structure of the particles. In order to provide further insight into the structure of nanoparticles in the 5 nm size regime formed by helium droplet synthesis we present selected high-resolution images in Figure 3. The shown particles have been produced in a previous series of experiments under similar helium droplet source conditions, however, the size of the shown particles and, in particular, the Ag:Au composition is the same as in the present study. Further details about the structure of nanoparticles comprising a Ag:Au ratio of 1:1 can be found in reference [20] (and the Supplementary Information of Ref. [20]). The shown images in Figure 3 correspond to high-angle annular dark-field (HAADF) images recorded by a high-resolution scanning transmission electron microscope (HR-STEM). The Ag:Au ratios correspond to 2:1 (red frame, a), 1:1 (green frame, b) and 1:2 (blue frame, c). The HAADF image intensity is proportional to the square of the atomic number ($Z^2$) [35]. Consequently, the image contrast within an individual nanoparticle represents zones that are rich of Ag (dark) or Au (bright).

It can be seen from the images in Figure 3 that even for the lowest Au doping level (Ag:Au of 2:1) a faint bright Au layer is visible at the surface (marked by red arrows). Consequently, it is concluded that even in the sub 5 nm size regime the helium droplet synthesis allows for the deposition of nanoparticles with a core@shell structure with extremely thin shell layers.

The optical properties of the prepared nanoparticles, deposited for 4 h each onto fused silica substrates, have been characterized employing UV/vis absorption spectroscopy. The recorded spectra are shown in Figure 4. Plain Ag (blue) and Au (red) nanoparticles serve as a reference, both exhibiting the characteristic LSPR of small, spherical nanoparticles on fused silica [11,36] peaking at 447 nm for Ag and 555 nm for Au. The figure also features spectra of deposited core@shell nanoparticles with Ag:Au ratios adjusted to 1:2 (orange), 1:1 (black) and 2:1 (green). Only a single LSPR peak is observed, which becomes increasingly red-shifted with increasing Au content, accompanied by decreasing intensity. For high Ag concentration (Ag:Au of 2:1) the LSPR feature resembles the Ag resonance, red-shifted to 484 nm. For medium (1:1) and high Au content (1:2) the red-shift is stronger and the LSPR peak maxima are found at 499 nm and 518 nm, respectively.

Previous studies on bimetallic Ag–Au nanoparticles relied on different preparation processes such as coating of the core metal using radiation chemistry [13], laser ablation [16], or solution phase synthesis [15,17,18]. Measured absorption spectra indicated that core@shell nanoparticles exhibit two plasmon resonances, one close to the resonance of the pure Au particle and one close to the resonance of the pure Ag particle. It required the transformation into an alloy state to obtain continuous shifts of the then single resonance between the pure Au and Ag absorption wavelength, the shift depending on the Au/Ag molar ratios.
cluster with 10 closed shells consisting of 2869 has 812 surface atoms, which corresponds to a surface to volume ratio of about 1:2.5. Thus, in this idealized scenario a Ag@Au core@shell particle consisting of 2869 atoms in total with a Ag:Au ratio of 2:5:1 could be surrounded only by one atomic monolayer of Au. From this estimation it becomes evident that at lowest Au doping levels the shell layer is extremely thin, in agreement with the nanoparticle shown in Figure 3a. This represents an interesting situation, where common theoretical models for the calculation of plasmon resonances that predict two disjunct peaks in the spectrum for core@shell nanoparticles [37,44] may cease to be valid as properties such as surface roughness, surface diffusion and atomic interdiffusion processes become important [45]. Furthermore, at around 5 nm various different cluster structures and morphologies become possible [25], which deviate from the idealized models.

Having characterized the nanoparticles and their optical properties, we can now proceed to analyze their capabilities as substrates for surface-enhanced Raman spectroscopy (SERS). Therefore, the nanoparticles deposited on fused silica substrates were functionalized with 4-methylbenzenethiol (4-MBT). The Raman spectra obtained for plain Ag and Au nanoparticle substrates as well as for bimetallic particles are shown in Figure 5 for three different Raman laser wavelengths. Note that the Ag spectra for 532 nm and 633 nm in Figure 5 have been scaled by x0.2 and the 532 nm Au an Ag@Au 1:2 as well as the 473 nm Ag@Au 2:1 spectra have been scaled by x2.5.

From near-edge X-ray absorption fine structure (NEXAFS) spectroscopy it is known that the sulfur atom, situated at one end of the molecule, binds to the surface (in the ideal case of a planar Au(111) surface the benzene ring is tilted by 33° with respect to the surface) [46,47]. Furthermore, 4-MBT is known to form self-assembled monolayers on both Ag and Au surfaces [48].

The Raman spectrum in Figure 5 can be readily assigned based on comparison to literature [34,49]. The most intense peak at 1080 cm\(^{-1}\) corresponds to a combination of a phenyl breathing mode, a CH in-plane bending and CS stretching (7a vibrational mode). The intense peak at 1595 cm\(^{-1}\) corresponds to a phenyl ring stretching mode (8a vibrational mode). The three peaks in between these two intense features at 1182 cm\(^{-1}\), 1378 cm\(^{-1}\) and 1486 cm\(^{-1}\) as well as the peak at 1698 cm\(^{-1}\) are assigned to in-plane phenyl ring vibrations. The broad structures observed in the left panel (473 nm) of Figure 5 for the three top most spectra and for the top spectrum in the middle (532 nm) panel correspond to residuals from the fused silica substrate, only the sharp lines are associated with signals from molecules.

Enhancement factors have been determined for the strongest Raman mode at 1080 cm\(^{-1}\) and are listed in Table 2. Note that the Raman enhancement factors have been determined by averaging over a 500 \(\mu m \times 500 \mu m\) area. Considering that the particles are close enough to coagulate, hot-spots between nearby nanoparticles are, presumably, present on the substrate, boosting the observed enhancement factors. It can be seen that the Ag nanoparticle substrate, which also exhibits the most intense LSPR, shows the highest enhancement. In general,
Fig. 5. Raman spectra recorded for the different nanoparticles functionalized with 4-methylbenzenethiol (4-MBT) molecules obtained by employing three different Raman laser wavelengths of 473 nm (blue), 532 nm (green) and 633 nm (red). The Raman spectrum obtained from 4-MBT attached to core@shell nanoparticle substrates with Ag:Au ratios of 2:1, 1:1 and 1:2 are shown together with spectra obtained from substrates consisting of plain Au and Ag particles.

Table 2. Enhancement factors determined for the Raman mode at 1080 cm\(^{-1}\) for nanoparticle substrates comprising Ag:Au ratios of 2:1, 1:1 and 1:2 as well as for the plain Ag and Au nanoparticle substrates.

| Ag:Au   | 473 nm | 532 nm | 633 nm |
|---------|--------|--------|--------|
| 1:0     | 1800   | 24000  | 30000  |
| 2:1     | 200    | 2100   | 6300   |
| 1:1     | 70     | 1700   | 12000  |
| 1:2     | Bld*   | 800    | 5800   |
| 0:1     | Bld*   | 300    | 5500   |

*Bld: below limit of detection.

the enhancement factors are lowest for the blue laser (473 nm) and highest for the red laser (633 nm). The enhancement factors for the bimetallic substrates are situated in between the pure Ag and Au nanoparticle substrates, where the Ag@Au nanoparticles comprising a 1:1 Ag:Au ratio show the next highest enhancement after the pure Ag nanoparticles. Note that the position of the LSPR maximum (which may be affected by the functionalization with 4-MBT \[50\]) does not necessarily have to coincide with the wavelength for maximum Raman enhancement \[51\], in particular, for substrates where individual nanoparticles are not completely isolated from each other.

An interesting aspect of the Raman spectra is the dependence of the Raman bands at 1595 cm\(^{-1}\) and 1698 cm\(^{-1}\) on the nanoparticle substrate, which differ greatly between the case where the molecules are attached to a Au or a Ag surface. For 4-MBT on Ag it is known that the peak at 1595 cm\(^{-1}\) shows a characteristic asymmetry \[34\]. The origin of this effect is still under debate but it may either be caused by a broadening of the 8a mode or a selective enhancement of the 8b mode, located about 15 cm\(^{-1}\) below. However, on Au substrates this effect is absent \[49\]. Furthermore, the 1698 cm\(^{-1}\) mode is only significantly enhanced for the Ag substrate \[49\]. Figure 6 shows a zoom into the corresponding region. It can be seen that the spectra gradually change their character from plain Ag to plain Au character with increasing Au shell thickness. Only when multiple Au shell layers are present (Ag: Au of 1:2, orange spectrum) the spectrum resembles the one obtained for molecules attached to plain Au nanoparticles. This indicates that even if coagulated, larger particles are formed on the glass substrate and contribute to the signal, in the case of nanoparticles with a Ag: Au ratio of 1:2 they are still covered by a fully closed Au shell.

4 Conclusions

The present work demonstrates the capabilities of the helium droplet synthesis approach for the production
of small plasmonic nanostructures. It is shown that for deposited Ag@Au core@shell nanoparticles, with diameters of about 5 nm, the spectral position of the localized surface plasmon resonance can be controlled by the Ag: Au ratio, which has been adjusted to 2:1, 1:1 and 1:2. Furthermore, upon functionalization with 4-MBT molecules, the nanostructures prepared from these nanoparticles are shown to be suitable substrates for surface-enhanced Raman spectroscopy (SERS). Raman enhancement factors determined for the 1080 cm$^{-1}$ mode are on the order of $10^3$–$10^4$. The Raman spectroscopy results further reveal that only particles with highest Au concentration (Ag: Au of 1:2) exhibit the signature of a plain Au shell.

In the present work we demonstrate the helium droplet synthesis approach for the production of plasmonic nanoparticles and nanosubstrates with the standard plasmonic materials, Au and Ag as well as bimetallic Ag@Au particles. However, in general the pickup technique allows choosing from a large variety of possible dopant materials. Moreover, the production method allows to produce small core@shell clusters without any chemistry involved, while the 5 nm size does not even represent a lower limit. The production method allows to produce small nanoparticles with increasing Au shell thickness.

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**Author contribution statement**

All the authors were involved in the preparation of the manuscript. All the authors have read and approved the final manuscript.

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**Fig. 6.** Zoom into the (normalized) Raman spectrum obtained with the 532 nm laser in the region of the 1595 cm$^{-1}$ and 1698 cm$^{-1}$ modes, which are sensitive to the substrate. It can be seen that the spectra gradually change their character from the case of molecules bound to plain Ag towards plain Au nanoparticles with increasing Au shell thickness.
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