Shell-Isolated Au Nanoparticles Functionalized with Rhodamine B Fluorophores in Helium Nanodroplets

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ABSTRACT: Nanoparticles consisting of three different materials in a layered core@shell@shell structure are synthesized in cold helium droplets by sequential doping. Upon the formation of Au core particles, a first shell layer is formed by adding either Ar, isopropyl alcohol, or hexane. Subsequently, the droplets are doped with rhodamine B (RB) molecules; fluorescence spectra recorded upon laser excitation at 532 nm provide insight into the structure of the formed complexes. For the two-component Au@RB system, the RB fluorescence is quenched in the presence of the Au core. If an intermediate isolating shell layer is introduced (Au@shell@RB), the fluorescence increases again. The results demonstrate that shell-isolated nanoparticles can be formed inside He nanodroplets and functionalized in situ with additional molecules. As the structure of the particles depends on the pickup sequence, the approach can be exploited for the synthesis and investigation of a large variety of different combinations of plasmonic metals, intermediate layers, and molecules.

The merging of plasmonics and spectroscopy resulted in a fruitful symbiosis from which many applications have emerged, ranging from plasmon-enhanced fluorescence (PEF) and surface plasmon resonance (SPR) spectroscopy to tip- and surface-enhanced Raman spectroscopy (TERS and SERS, respectively).1−7 About a decade ago, the versatility of methods based on plasmonic materials was greatly expanded by the introduction of shell-isolated nanoparticles (SHINs).8 These particles consist of a plasmonic metal covered by a chemically inert shell layer, which avoids particle agglomeration and direct contact between probe molecules and metal.9−11 Considering the widespread applications, an understanding of the interactions between different plasmonic metal nanoparticles and molecules is very important. Here, we introduce helium droplet synthesis as a new bottom-up approach for the formation and investigation of such systems, consisting of plasmonic nanoparticles covered by a shell layer and surrounded by fluorophore molecules.

The optical properties of Cu12 and Ag13 nanoparticles as well as Au oligomers14 inside helium droplets have been studied previously. For spherical Ag particles in small helium droplets, the localized surface plasmon resonance (LSPR) at about 3.8 eV has been observed. With increasing droplet size, the presence of quantum vortices15,16 along which dopants preferentially agglomerate, leads to the formation of metal nanowires.17−19 The transition from compact isolated nanoparticles to elongated wire structures goes along with the emergence of additional plasmon modes in the visible and infrared, characteristic for nonspherical structures.20 The LSPR of deposited nanoparticles formed by helium droplet synthesis has been investigated for the Ag@Au system.21,22

Infrared spectroscopy of Ag particles covered with shells of ethane,23 methane, ethylene, and acetylene24 revealed the formation of solid-like (or glassy for ethane) layers around the Ag core in the cold He droplet environment. Here, we show that such a layer can be used as a spacer between fluorophore molecules and a metal particle, a configuration similar to shell-isolated nanoparticle structures.3,25−29 Thereby, the cold (0.4 K) He superfluid environment allows for the use of unconventional isolation layers (argon, isopropyl alcohol, and hexane), which are combined with rhodamine B fluorophores and Au core particles. The results demonstrate that triple-layer systems can be formed in helium droplets and open up new opportunities for the combination of different materials in the inert helium droplet synthesis environment.

Core@shell@shell particles are formed by the successive capture and coagulation of dopants in three different pickup regions,30 as sketched in Figure 1. The He droplets are first doped with Au atoms, which agglomerate and form spherical or elongated wire-like metal particles, depending on the initial He droplet size and the pickup oven temperature.31

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constant Au and RB oven temperatures. The red laser, resonant to the π−π* transition. With increasing oven temperature, a red-shift of the peak is observed. While at high temperatures the peak form is very similar to RB thin films or RB in solution, at a low doping level, the spectrum is more similar to the spectra of gas-phase molecules. (see Supporting Information (SI), Figure S6 for a comparison to literature spectra). The observed variation of the peak position from 550 to 593 nm is explained as follows: At low oven temperatures, the number of molecules per droplet is small, and large complexes cannot be formed. In particular, if multiple vortices are present, as expected at the employed droplet sizes, molecules may be attached to them at different sites, giving rise to a free-molecule-like fluorescence due to the only weak perturbation by the droplet environment. With increasing doping level, RB molecules start to coagulate, which goes along with a more thin-film- or solution-like fluorescence. Thus, the observed change in the spectra with increasing doping level is interpreted as an evolution from isolated molecules or small complexes pinned to vortices to a regime where RB molecules are agglomerated and form large elongated wire structures.

The results presented in the following are obtained at a constant RB oven temperature of about 230 °C, a temperature at which degradation effects due to the thermal decomposition of molecules do not affect the LIF signal (see Experimental Methods for details). At this temperature, the fluorescence peak is located at about 586 nm.

Figure 2 shows three dispersed LIF spectra of Au@RB core@shell particles recorded for different Au oven temperatures, while the RB temperature is kept constant. Note that at 600 °C, Au doping is negligible, and the spectrum provides a reference that corresponds to bare RB complexes. It becomes evident that the shape and position of the fluorescence spectrum is almost unaffected by the presence of the Au particles; only a weak blue-shift of about 2 nm is observed. However, the signal intensity decreases significantly with increasing Au amount. The results have been obtained for large droplets (d ≈ 800 nm) that host vortices. For Au, it has been shown that in this case, small isolated Au particles are formed at low doping levels, whereas elongated nanowires, pinned to vortices, are present at high doping levels. For the recorded spectra, this implies that at low doping levels, small spherical Au clusters are present prior to RB doping, while at high oven temperatures, Au nanowires are present, to which RB molecules can attach. Furthermore, in the synthesis of multilayered structures in helium droplets, one has to keep in mind that for every atom that is added, the droplet size is reduced by the evaporation of He atoms in order to dissipate the excess binding energy. By this mechanism, the droplets can keep their temperature at 0.4 K constant; however, it also causes a reduction of the geometric cross section and limits, thus, the amount of shell material that can be added to a core particle. Consequently, in the absence of any additional effects, one would expect a continuous decrease of the fluorescence yield with an increasing amount of Au core material for a constant RB oven temperature.

To investigate the effect of the Au core on the fluorescence in more detail, the total RB fluorescence yield as a function of the Au oven temperature is shown in Figure 3. Each data point has been obtained by integrating the recorded LIF spectrum from 530 to 750 nm. We start the discussion with Au@RB core@shell particles in large helium droplets (6 K nozzle temperature, d ≈ 800 nm). As soon as Au is present, the fluorescence is quenched, reflected by the rapid decrease of the fluorescence with increasing Au temperature. Fluorescence quenching is very typical for fluorophores directly attached to a metal surface. Au nanoparticles are known to be efficient

Figure 1. Sketch of the helium drop synthesis process. Tripple-layered particles are formed by sequential doping and analyzed by laser-induced fluorescence (LIF) spectroscopy.

Subsequently, either Ar, isopropyl alcohol (iPrOH), or hexane is added. The last pickup cell passed by the droplet beam holds rhodamine B (RB) molecules.

We start the discussion with bare RB molecules isolated in helium droplets. Figure 2a shows LIF spectra recorded for RB in large helium droplets (d ≈ 800 nm) as a function of the RB oven temperature, (b) spectra recorded for different Au oven temperatures at a constant RB doping level, (c) hexane@RB core@shell particles for different hexane doping pressures (no Au doping), and (d) Au@hexane@RB particles for different hexane doping levels and constant Au and RB oven temperatures. The red “hexane+” spectrum has been recorded at a higher hexane partial pressure than the yellow “hexane” spectrum.

Figure 2. Dispersed LIF spectra recorded using large helium droplets (~800 nm diameter): (a) bare RB, fluorescence as a function of the RB oven temperature, (b) spectra recorded for different Au oven temperatures at a constant RB doping level, (c) hexane@RB core@shell particles for different hexane doping pressures (no Au doping), and (d) Au@hexane@RB particles for different hexane doping levels and constant Au and RB oven temperatures.
quenchers for fluorescent dyes; in particular, fluorescence quenching has been observed for RB molecules adsorbed on citrate capped Au nanoparticles. This observation indicates that the molecules are in contact with the metal core inside the helium droplet, i.e., core@shell Au@RB structures are formed. The fluorescence decreases continuously up to about 1150 °C, a temperature where the helium droplets are still only sparsely doped. Interestingly, the fluorescence recovers and shows a local maximum at 1280 °C. At this point, the He droplets have only lost about 5% of their volume, as estimated from the He background pressure. The final decrease of the fluorescence yield beyond 1280 °C is attributed to the continuous shrinking of the He droplets with increasing Au doping. This correlation between droplet beam attenuation and fluorescence decrease is discussed in more detail in the SI (Figure S7). The black curve shows the same experiment but for small He droplets (10 K nozzle temperature, d ≈ 80 nm), in which spherical (<5 nm) Au particles constitute the core material. The trend is similar in this case: a rapid monotonic decrease is observed with only a weak shoulder at about 1100 °C.

In the case of large He droplets, the fluorescence enhancement with respect to the local minimum is attributed to the structural change from individual small Au clusters to connected nanowires with increasing pickup level. Small separated Au clusters have a larger surface area than elongated wire structures despite the fact that there are more metal atoms present in the second case. If the Au surface decreases, fewer RB molecules can attach to the Au, and thus, the number of particles affected by surface quenching is lower. For small droplets, this effect is also present but not as pronounced, because long elongated wires are not formed. A significant plasmon-enhancement effect is not expected due to the close proximity between molecules and metal. However, for Au nanoparticles, it has been shown that only particles larger than about 2 nm support an LSPR due to quantum confinement effects. Thus, the emerging LSPR may contribute to the signal with increasing Au particle size.

A common approach to reduce the fluorescence quenching in metal–molecule systems is based on the insertion of a nonconducting dielectric layer between the metal and fluorophore. The resulting structures are referred to as shell-isolated nanoparticles (SHINs). This requires the formation of triple-layer nanoparticles, which has so far not been realized with the helium droplet approach. In order to demonstrate this concept, we use a third pickup cell mounted between the Au and RB pickup regions. In our current experimental setup, geometrical restrictions allow only for the implementation of a cell that holds gaseous species; however, in principle, a large variety of dopants can be used as a shell layer if a third high temperature oven is installed. Thus, Ar, iPrOH, and hexane have been employed as spacer material, all of which are expected to form a solid shell layer around the Au structures inside the droplets at 0.4 K. If the configuration results indeed in Au@hexane@RB, Au@iPrOH@RB, and Au@Ar@RB core@shell@shell nanoparticles, the intermediate layer will separate the molecules from the metal, thereby, reducing the effect of fluorescence quenching.

It is instructive to start the discussion with the spectra of hexane@RB nanoparticles without the Au core, which are presented in Figure 2c, recorded without hexane (blue), with low hexane (orange), and heavy hexane (red) doping. It can be seen that the addition of a hexane “core” is accompanied by an increasing blue-shift and a decrease of the fluorescence yield. The latter is explained by the shrinking of the He droplet upon doping with hexane.

Figure 2d shows spectra for hexane concentrations comparable to Figure 2c but with an additional Au core. Comparing the spectra with (orange) and without (blue) hexane shows that the presence of the isolation layer enhances the total fluorescence yield. This observation indicates that inside a helium droplet, the addition of hexane leads to the formation of an intermediate spacer shell that inhibits direct contact between RB and Au metal. However, the enhancement goes along with a prominent blue-shift. At heavy hexane doping levels, the shrinking of the He droplets due to the hexane doping dominates, and the spectrum is very similar to the one without a Au core (red spectrum, Figure 2c).

The green trace in Figure 3 shows the effect of moderate hexane doping on the integrated fluorescence yield of Au@hexane@RB structures in large He droplets as a function of Au oven temperature. In contrast to the Au@RB traces, an immediate quenching is not observed upon Au doping, indicating that the RB molecules do not get in contact with the metal surface if hexane is present. The signal remains fairly constant and starts to decrease beyond 1300 °C where the effect of the decreasing droplet size, i.e., pickup cross section, takes over. An increase of the fluorescence with respect to the base level, however, is not observed, similar to previous experiments on RB molecules attached to Au particles in solution. In the case of small molecule–particle separation, the overlap of the Au LSPR with the RB emission enables an effective energy transfer from the molecule to the Au particle, reducing the RB fluorescence. For very small particles, the energy transfer proceeds through nanosurface energy transfer (NSET) (non-Förster energy transfer).

Figure 4 shows a series of experiments with Au@spacer@RB particles using three different spacer materials: iPrOH, Ar, and hexane. The amount of spacer molecules is continuously increased by slowly opening a leak valve connected to a reservoir that holds the molecules in the gas phase. In this series of experiments, the doping conditions for Au and RB are kept constant. At the position marked by the dashed line, the valve is closed again, and the pressure in the intermediate pickup cell slowly decreases again. Each red data point corresponds to the integrated fluorescence yield (530 to 750 nm). It can be seen that all three spacer materials show the same behavior, i.e., the fluorescence yield is first enhanced and...
Each spacer material appears unlikely. In the presence of the 0.4 K He droplet temperature. The yield increases by a factor of 1.5. This may be explained by differences in the interaction between spacer molecules and RB. In additional measurements, presented in the SI (Figure S2), it has been confirmed that this behavior is only observed for core@shell@shell nanoparticles where the metallic core is present, i.e., hexane@RB particles do not show any enhancement. For small three-layered spherical nanoparticles, the same effect as in Figure 4 is observed (see also SI, Figure S3).

The blue data points correspond to the fluorescence peak position (emission maximum). Without a spacer, the peak position is located at about 586 nm. Interestingly, the peak position (emission maximum). Without a spacer, the peak position is located at about 586 nm. As the behavior is similar for all three cases; the shift is continuous and reaches a minimum at about 550 nm. As the behavior is similar for all three cases; the shift is continuous and reaches a minimum at about 550 nm. For small triple-layered spherical nanoparticles, the same effect as in Figure 4 is observed (see also SI, Figure S3).

The blue data points correspond to the fluorescence peak position (emission maximum). Without a spacer, the peak position is located at about 586 nm. Interestingly, the peak shifts monotonically to the blue with an increasing doping level, independent of the spacer material. At the fluorescence yield maximum, the peak is blue-shifted by about 15 nm in all three cases; the shift is continuous and reaches a minimum at about 550 nm. As the behavior is similar for all three molecules, a typical solution shift, which would be different for each spacer material, appears unlikely. In the presence of an isolating shell layer, the surface to which RB molecules can attach is larger, and thus, they are more separated from each other. Furthermore, the orientation of the molecules with respect to each other and the metal surface can change. Thus, structural effects may explain the variation of the peak position. However, the peak shift is evidently related to the spacer material, because the same behavior is observed in the absence of the Au core (Figure 2c).

In this manuscript, we show that triple-layer core@shell@shell nanoparticles can be formed inside He droplets by the sequential addition of different dopants. Rhodamine B molecules are employed as fluorophores, and the recorded laser-induced fluorescence (LIF) spectra provide insight into the configuration of the core and shell layers inside the droplets. In the presence of Au core particles, fluorescence quenching is observed, similar to dye molecules attached to Au nanoparticles in solution. If an intermediate shell layer is inserted between the Au core and RB molecules, the fluorescence increases again. This behavior is observed for three different spacer molecules, hexane, iPrOH, and Ar, all of which are expected to be solid at the 0.4 K He droplet temperature. This indicates that the additional intermediate layer acts as an isolating shell that separates the metal from the RB molecules. It is, thus, concluded that core@shell@shell nanoparticles are formed inside He droplets, similar to shell-isolated nanoparticles (SHINs) that are used in surface-enhanced spectroscopy methods.

In the case of Raman spectroscopy, fluorescence quenching is advantageous, as it eases the detection of Raman scattered light. Thus, by exploiting plasmonic enhancement, it may become possible to employ Raman spectroscopy as a new analysis tool to probe molecules and nanoparticles in helium droplets.

Considering that helium droplets can be doped with a large variety of materials, systematic studies of different molecule, spacer, and plasmonic metal combinations may lead to new materials with potential applications in sensor technologies or biomedicine.

### EXPERIMENTAL METHODS

The nanoparticles are synthesized in helium droplets by sequential pickup of dopant atoms and molecules; the employed apparatus is described in detail in ref 47. Rhodamine B from Radiant Dyes Laser GmbH, Au pellets (99.9%) from Ogsusa GmbH, Ar gas (99.999%) from Tega GmbH, and isopropyl alcohol (99.7%) from Merck GmbH are used as doping material without further treatment.

The expansion of He (99.9999%, from Air Liquide Austria GmbH) at a pressure of 60 bar through a 5 μm nozzle at 6 and 10 K results in He droplets with an estimated diameter of about 800 and 80 nm, respectively, corresponding to ~1 · 10^10 and ~7 · 10^8 He atoms per droplet.29,48 The droplet beam passes two pickup ovens, the first loaded with Au metal and the second holding rhodamine B (RB) powder. The RB oven is kept below 245 °C to prevent thermal decomposition, except for the temperature study presented in Figure 2b, during which 260 °C has been reached. If the RB temperature is kept at such a high temperature for time scales on the order of hours, a degradation of the molecules is observed in the form of a continuous decrease of the LIF signal intensity. Furthermore, the RB powder in the pickup oven was replaced after each series of experiments. The RB pickup has been investigated in more detail; time-of-flight (TOF) mass spectra are presented and discussed in the SI (Figure S1). A strong RB parent peak is observed, indicating intact molecules after evaporation. The RB oven temperatures stated in the manuscript are estimated based on the heating current and the oven resistance. For Au, the melting plateau is visible in LIF spectra recorded as a function of the Au oven temperature, providing a reference point for the Au temperature scale. The corresponding spectra in the main manuscript are calibrated and have been obtained by the procedure described in the SI (see Figure S5).

A gas pickup cell is mounted in between these two ovens, allowing for doping with a third species that can be introduced via a precision leak valve. This setup requires that the intermediate dopant is either gaseous or that it can be easily evaporated, which is the case for the used species hexane, Ar, and iPrOH.
Two different droplet sizes (nozzle temperatures) have been chosen in order to access different nanoparticle sizes and shapes. At a nozzle temperature of 6 K, large elongated nanoparticle structures can be formed inside helium droplets, consisting of more than $10^3$ dopants. At 10 K, spherical structures are formed, consisting of several hundreds to thousands of dopants with diameters up to 5 nm.31

The prepared particles are analyzed in situ under UHV conditions by dispersed laser-induced fluorescence (LIF) spectroscopy in a separately pumped chamber using a Kymera 328i spectrograph equipped with a cooled iDus 401 CCD camera (−100 °C). An edge filter (Semrock S32 RazorEdge) is used for laser stray-light suppression. The entry slit opening of the spectrograph has been set to 150 μm, and a 150 lines/mm (500 nm) diffraction grating was used. All spectra were captured with a 20 s acquisition time. A Coherent Verdi V18 provides S32 nm continuous-wave laser light to excite the RB molecules; S W (focus diameter $≈$ 0.5 mm) has been employed in the experiments (see SI, Figure S4, for laser power and saturation studies).

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