Deliverable 3.2:

Synthesis of functionalized nanoparticles with $m > 10^5$ amu

Objectives and Description of Tasks

Synthesis of size-selected nanocrystals with large masses ($m > 10^5$ amu) and suitably functionalized to bring them into the "gas-phase" is a principal task of UNIBAS. UNIVIE will test these compounds with regard to their intact volatilization, single photon neutralization and detection. UNIBAS will further modulate the absorption and fluorescence properties of the nanocrystals to maximize the detection efficiency in experiments at UNIVIE. UNIVIE will explore acoustic and thermal laser desorption to launch the nanoparticles.

Controlled synthesis of nanoparticles beyond 10^5 amu

We are working on the synthesis of nanocrystals with optimized volatilization features. Our current strategy is based on reducing the van der Waals interactions of the crystals by functionalizing them with perfluoroalkyl chains. In a first approach UNIBAS synthesized gold nanoparticles in the mass range of 10^4 - 10^5 amu stabilized with perfluoroalkyl ligands (F1-AuNPs) (Fig. 1).

Fluorocarbon-coated gold nanoparticles were obtained by reduction of $HAuCl_4$ (0.309 g, 0.91 mmol) in 10 mL of ethanol in presence of the ligand 1H,1H,2H,2H-perfluorooctanethiol (**F1**) (0.692 mg, 1.92 mmol). Aqueous $NaBH_4$ was added dropwise to the above solution, and the mixture was vigorously stirred for 3h at room temperature. The yellow $AuCl_4$-solution immediately turned brown by the addition of $NaBH_4$, indicating the progress of reduction. After the stirring was stopped, black precipitates separated from colorless supernatants were collected by centrifugation. The black color of the precipitates indicates the formation of very small gold nanoparticles. To completely remove excess non-coordinating molecules, the solid was washed several times with different solvents until no unbound-ligand signal was detected by ^{1}H-NMR spectroscopy.

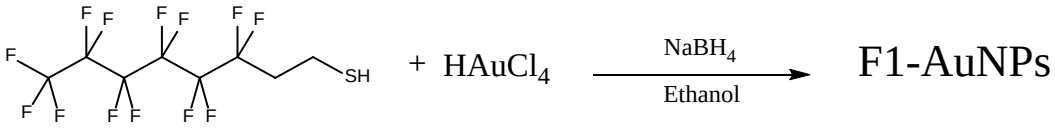

Figure 1. *Synthetic procedure of the perfluoroalkyl-gold nanoparticles, F1-AuNPs.*

As F1-AuNPs are completely insoluble in any solvent, ^{1}H- and ^{19}F-NMR and UV spectroscopy characterization was not possible. Although, the successful functionalization of gold nanoparticles with the perfluoroalkyl chains was confirmed by infrared (IR) spectroscopy (Fig. 2, left), as the spectra of the ligand and the nanoparticles show the same picks. Furthermore, NPs were also characterized by thermogravimetric analysis (TGA), MALDI-TOF mass spectrometry and transmission electron microscopy (TEM). TGA analysis (Fig. 2, right) shows up the thermal stability of the NPs until 90 ºC approximately. Around 57 % of the mass is lost around 250 ºC, that corresponds to the ligands desorption (boiling point of free ligand F1= 58ºC). Based on it, the estimated proportion of Au:F1 in the nanoparticles is 3:2 and the molecular formula is $[Au_3(C_8F_{13}H_4S)_2]_n$.

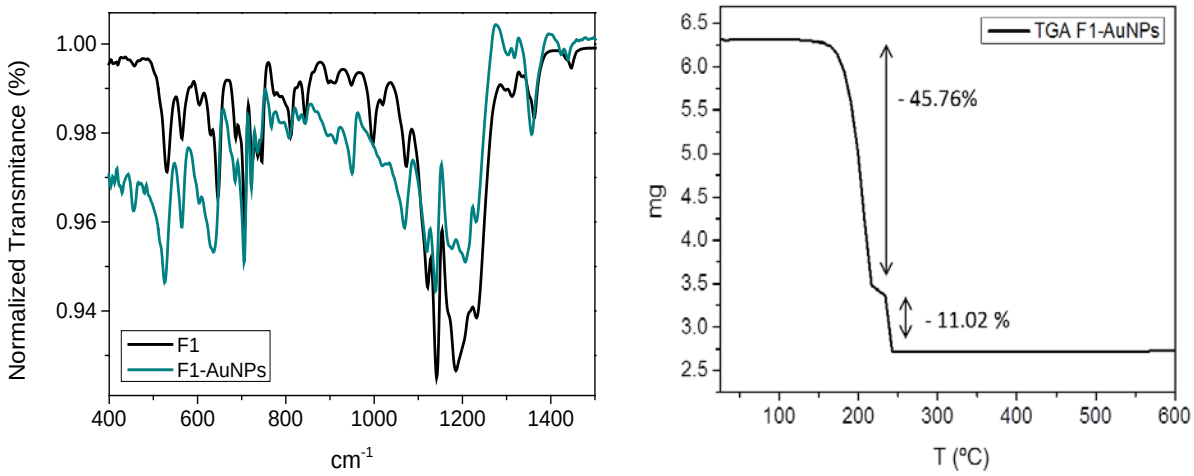

Figure 2. *IR spectra of F1 and F1-AuNPs (left) and TGA analysis of F1-AuNPs (right).*

The size and the mass of the NPs was characterized by HR-TEM and MALDI-TOF mass spectrometry, respectively (Fig. 3). We find a narrow size distribution of the nanoparticles with diameters around 1-2.5 nm and an average mass of 3×10^4 amu. The total mass spread between 30000 and 40000 amu. According to these results, it is possible to propose the molecular formula of $[Au_{78}(C_8F_{13}H_4S)_{56}]$ for the 35000 amu F1-AuNPs.

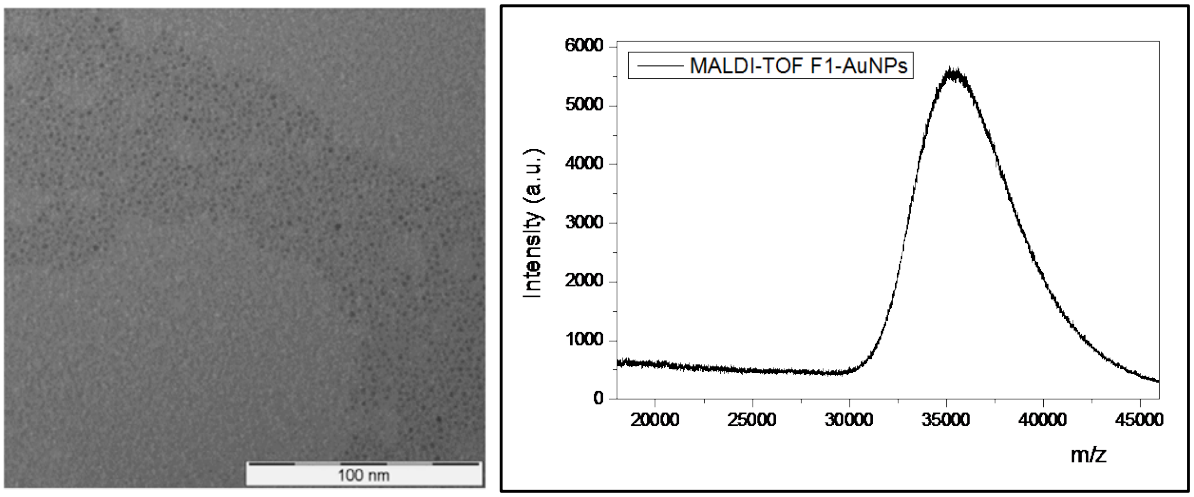

Figure 3. *HR-TEM image (left) and MALDI-TOF mass spectrometry (right) of F1-AuNPs.*

Before investigating their size-selective separation, their volatilization features were analyzed at UNIVIE. The AuNPs displayed decomposition temperatures clearly below their volatilization temperature. Only individual gold atoms could be detected. The AuNPs are thus rated as not suitable for the envisaged matter-wave diffraction experiments.

Conclusion

These AuNPs prove that the challenge of controlled synthesis of high-mass ligand-stabilized nanoparticles has been successfully met. In neutral desorption and post-ionization experiments at UNIVIE the gold nanoparticles seemed however largely to decompose.

New development based on the proposed experimental techniques

Our current efforts are geared towards synthesizing perfluororalkyl-coated silicon nanoparticles (SiNPs) which are expected to have superior stability features. Furthermore SiNPs comprise intrinsic optical properties, like tune-able absorption and fluorescence features, increasing the range of potential volatilization and detection techniques in the interference experiments.

Various synthetic approaches towards such SiNPs are currently investigated in details.

- Synthesis of a precursor based on SiNPs coated with a surfactant such as tetraocthylamonium bromide (TOAB) and the subsequent exchange of the coating ligand.
- Direct synthesis of the fluorinated-SiNPs by reducing $SiCl_4$ and the subsequent addition of the selected ligand.

Once a promising synthetic protocol is identified, we will investigate the potential diversity of stabilizing ligands in order to obtain series of monodisperse, massive and sublimable nanoparticles.

Laser induced thermo-mechanical stress to release nanoparticles in the 10^{10} amu mass range

Recent experiments on laser-induced acoustic desorption (LIAD) at UNIVIE, triggered by the goals of NANOQUESTFIT, also led to the insight that thermo-mechanical stress may break out nanoparticles from a clean silicon wafer surface. This source has been successfully used in a new demonstration experiment for cavity-assisted laser cooling. It showed for the first time the possibility of generating ultrahigh-mass particles (d≃ 300 nm, m≃ 10^{10} amu) at velocities in the range of 0.5-2 m/s in a clean ultra-high vacuum environment.

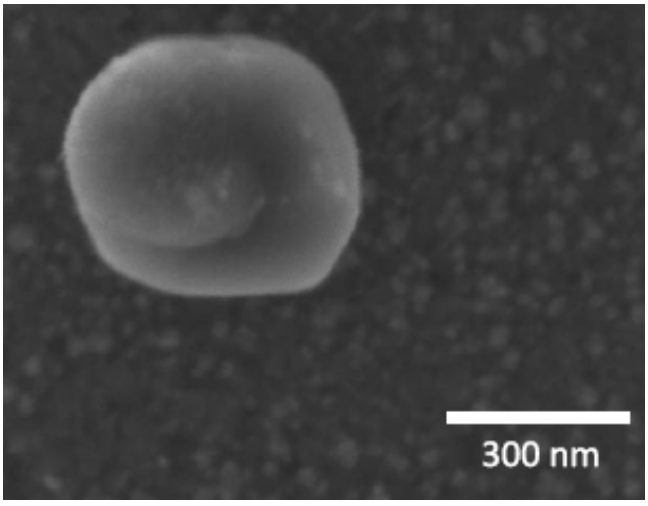

Figure 2: *SEM image of a pure silicon particle with a diameter of about 300 nm, for cavity-assisted cooling experiments. Cavity cooling is one promising road towards ultrahigh mass interferometry. Explorations of such sources therefore fall into the deliverables D1-for the last year of the project.*

These velocities are still too fast, the particles still too massive and too hot for imminent quantum interference experiments, but cavity-assisted optical cooling allowed us already to reduce the transverse kinetic energy of such particles by a factor of 30 [1].

This is a new and important step in a road map of future quantum experiments beyond 10^8 amu which we promised to deliver by the end of the project in 2015.

Conclusion

The AuNPs prove that nanoparticles can be synthesized. The pristine silicon nanoparticles have been launched even at masses way beyond our initial expectations, here beyond 10^{10} amu.

The deliverable can therefore be counted as successfully accomplished.

Outlook on synthetic nanoparticles

In order to achieve the goals of high-mass interferometry, further work is clearly needed. This will be pursued with silicon and silicon dioxide nanoparticles with and without tailored ligand shells. This and the ongoing synthesis of tailor-made functionalized multi-porphyrin systems are corner stones for the later deliverable **D4-3**, too.

Outlook on laser-induced break-off of nanoparticles

As a follow-up of this effort we are currently exploring the possibility of nanostructuring silicon wafers at TAU to fabricate arrays of nanoparticles which may be broken off in a controlled manner and at low velocity using laser shocks. This work contributes to the goal of launching slow and size-controlled objects in the ultrahigh mass range between 10^7 and 10^{10} amu at UNIVIE.

References

[1] P. Asenbaum, S. Kuhn, S. Nimmrichter, U. Sezer, M. Arndt, Nature Commun 4, 2743 (2013).