Gold nanoclusters investigated via femtosecond stimulated Raman spectroscopy

V. Svačinová[1*], M. Kloz[2], K. Šišková[1]

[1] Department of Experimental Physics, Faculty of Science, Palacký University Olomouc, 17. Listopadu 12, 771 46 Olomouc, Czech Republic

[2] ELI Beamlines, Za Radnicí 835, Dolní Břežany, 252 41, Czech Republic

*veronika.svacinova02@upol.cz

Abstract:

Gold nanoclusters (AuNCs) with diameter less than 2 nanometres have fluorescent properties. These nanoclusters can be prepared by microwave assisted synthesis using BSA (bovine serum albumin) as a template and, simultaneously, as a reducing agent as demonstrated in our previous study (1). During the synthesis, Au(III) ions are reduced to Au(II), Au(I), and/or Au(0) which are bonded to BSA forming thus Au(II)-BSA, Au(I)-BSA complexes and/or Au(0)NCs-BSA, respectively (2). From now on, we are going to use the general label AuNCs-BSA for all the species included within the samples in this study. Femtosecond stimulated Raman spectroscopy (FSRS) an ultrafast nonlinear optical technique is used to study vibrational structure of AuNCs-BSA for the first time here. FSRS has a time resolution comparable to the vibrational period of molecular movements (ps to fs) and energy resolution less than 10 cm^{-1}. Three laser pulses are exploited in a typical FSRS experiment: actinic pulse, Raman pulse and probe pulse (3).

Fig. 1: The first result from AuNCs-BSA FSRS measurements. There are signals from the cuvette and water, i.e., artefacts.

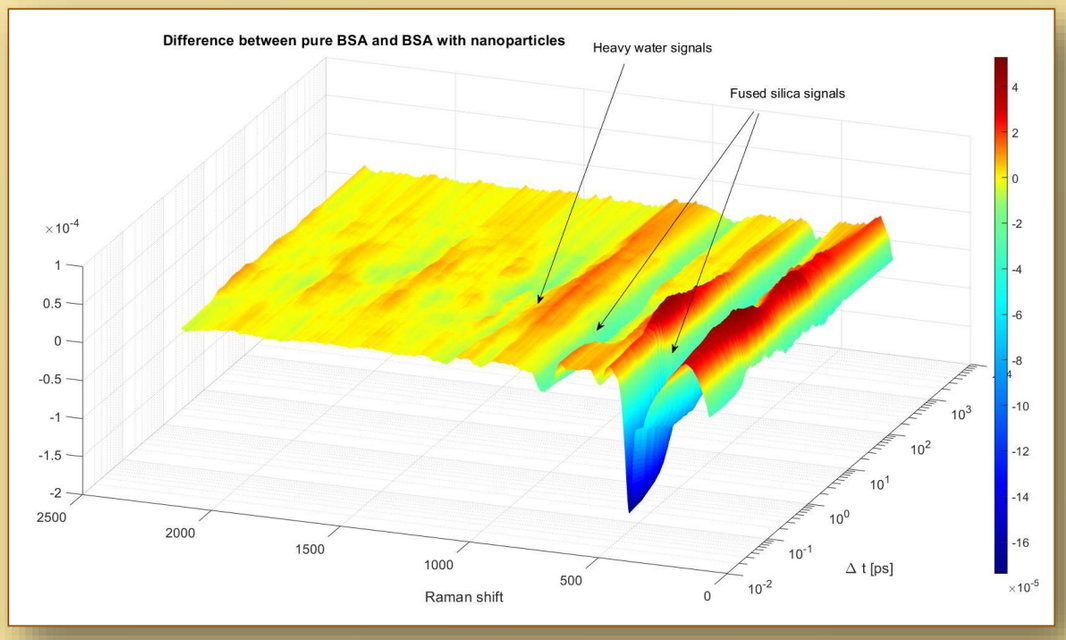


Fig. 2: Results of FSRS measurements in flat jet mode (without laser beam passing through the wall of a cuvette). BSA in water serves as a reference. Inset - a part of spectrum in the region where BSA peak dominates.

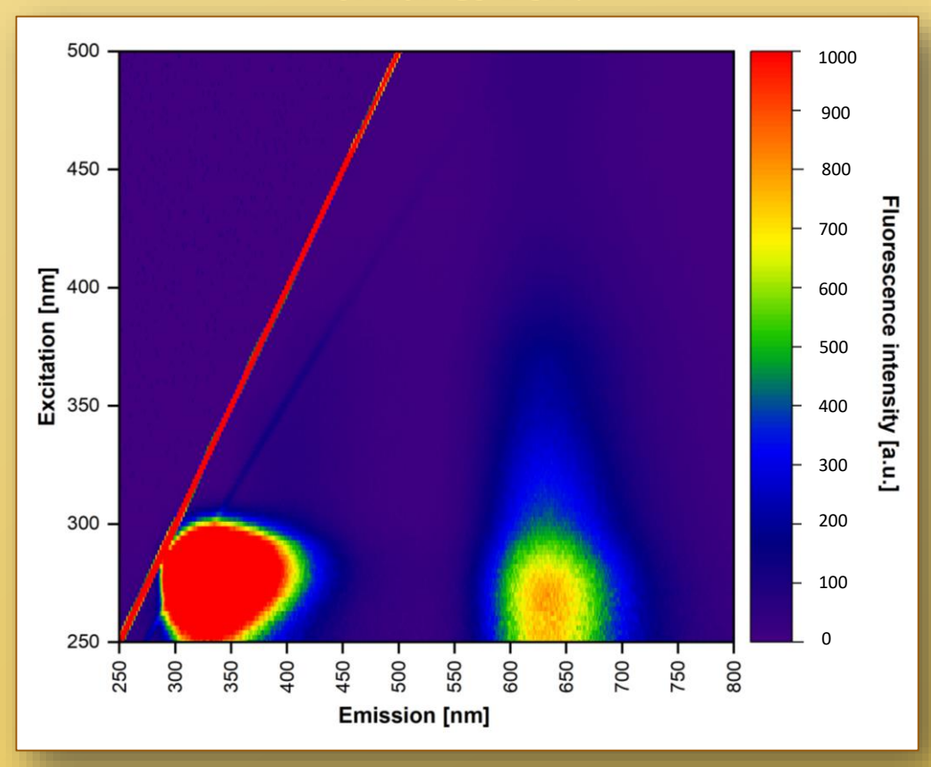
Chemicals: $HAuCl_4$; 98% BSA; NaOH; all purchased from Sigma-Aldrich

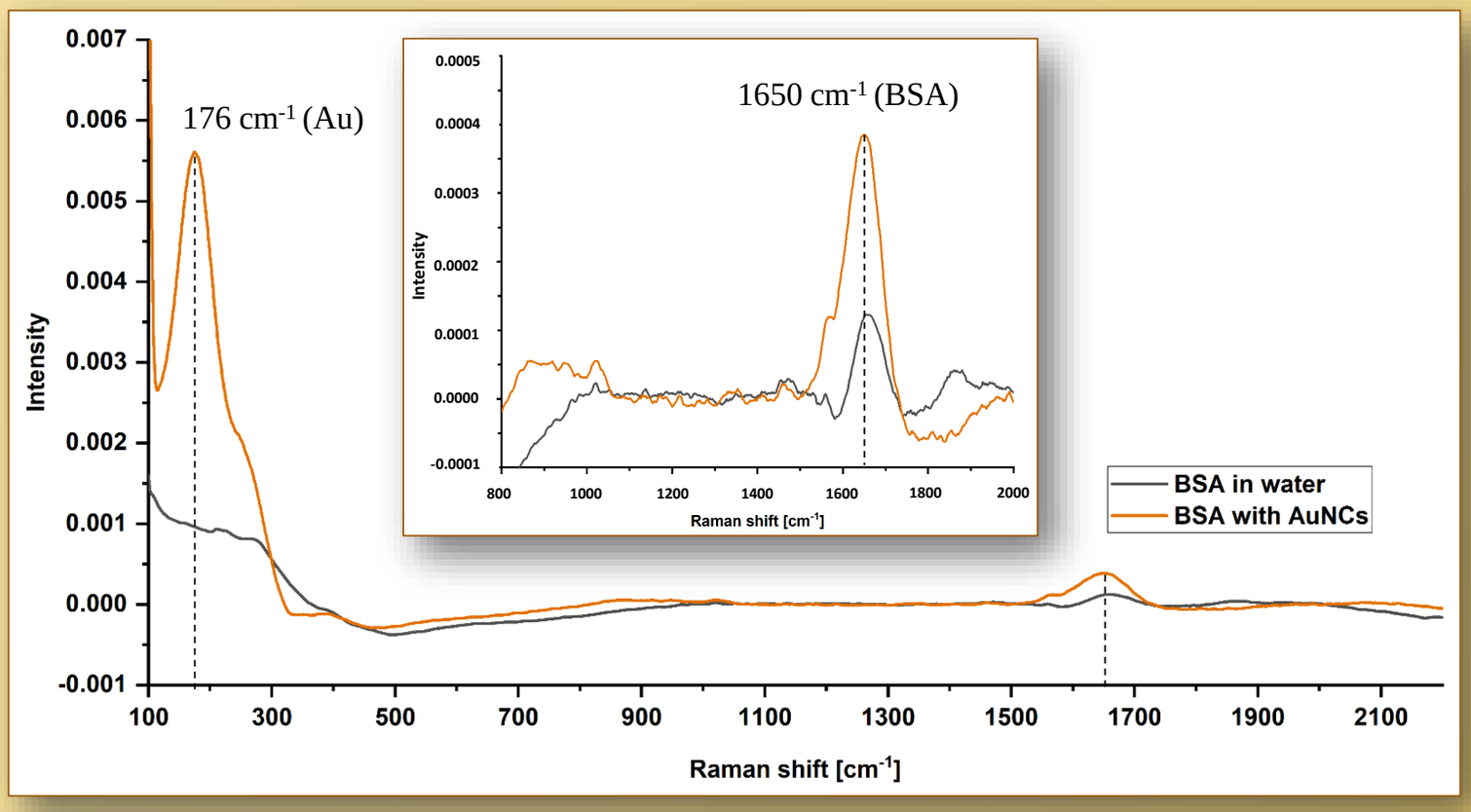
Methods of characterization: Femtosecond stimulated Raman spectroscopy (FSRS), steady-state fluorescence spectroscopy, dynamic light scattering (DLS), zeta potential measurements, UV-vis absorption spectroscopy.

Main-take home message:

AuNCs-BSA system was investigated via FSRS for the very first time. According to our results, two main peaks are observed in FSRS spectrum: 176 cm^{-1} belonging to Au and 1650 cm^{-1} attributable to BSA.

Fig. 3: Fluorescence 3D excitation/emission map of AuNCs-BSA.





Tab. 1: Zeta pontential values and particle size distribution expressed as average hydrodynamic diameter (determined by DLS, based on measurements of changes in light intensity as a function of time) for BSA and AuNCs-BSA. Percentual content of particular average diameter is given in parantheses.

Sample	Zeta potential	Average hydrodynamic diameter		
AuNCs-BSA	(-30.9 ± 1.1) mV	(31.7 ± 4.2) nm (51.9 %)	(6.2 ± 0.7) nm (26.3 %)	(213.6 ± 34.4) nm (21.8 %)
BSA	(-24.8 ± 0.9) mV	(142.6 ± 3.4) nm (100 %)		

Outlook:

FSRS seems to be a very promising tool in gaining new information about nanostructures of noble metals. However, the intensity of AuNCs-BSA signal in FSRS has to be improved. Therefore, the next step is to investigate gold nanoparticles with BSA on their surfaces (AuNPs-BSA). These AuNPs-BSA possess surface plasmon at 525 nm which can lead to FSRS intensity increase. Consequently, the combination of Au and Ag nanostructures could be investigated by FSRS.

References:

(1) P. Andrýsková et al., The effect of fatty acids and BSA purity on synthesis and properties of fluorescent gold nanoclusters. Nanomaterials 2020, 10, 343; doi:10.3390/nano10020343

(2) R. Ostruszka et al., Evidence of Au(II) and Au(0) states in bovine serum albumin - Au nanoclusters revealed by CW-EPR/LEPR and peculiarities in HR-TEM/STEM imaging. *under revisions in Nanomaterials*

(3) P. Kukura et al. Femtosecond Stimulated Raman Spectroscopy. Annu. Rev. Phys. Chem. 2007. 58:461–88

Acknowledgement:

This research was funded by Grant Agency of the Czech Republic, grant number 19-03207S, and by Internal Grant Agency of Palacký University, grants numbers IGA_PřF_2021_003 and IGA_PřF_2022_003.