PD Research Report for the 2017 year

Name（Research group）Beata Wrzosek

（Ozaki Research Group, Graduate School of Science and Technology）

Research Theme SERS blinking on anisotropic nanoparticles

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Research Results

The aim of the project was to study SERS blinking on anisotropic Ag nanoparticles. The whole work was divided on few steps:

1) *Synthesis of anisotropic Ag nanoparticles*
2) *UV-Vis and SEM/TEM study, calculation of shape distribution*
3) *Check if SERS blinking is possible on them*
4) *Analysis of results*
5) *Preparation of result for comparison with results of SERS blinking on spherical NP*

1) <u>Synthesis of anisotropic Ag nanoparticles</u>

The anisotropic nanoparticle was synthesized in seed mediated growth methods. The first step was the synthesis of small spherical nanoparticles – seeds, as follow:

10ml cold H_2O + 0.1 ml $AgNO_3$ (2.5 mM) + 0.1 ml CytNa(0.1 M)

+ cold $NaBH_4$ (25mM) in 20 drops x 0.01 ml

The next step was carried out with using of additional substrate: capping agent:

5ml **capping agents** (5mM)+ 0.05 ml $AgNO_3$ (25 mM)
+ 0.05 ml **seeds**

+ ascorbic acid (0.001M) in *few* portion of 0.1 ml

catch the moment of the color change

The chosen capping agent was cyclodextrine.

2) <u>UV-Vis and SEM/TEM study, calculation of shape distribution</u>

In the results of optimized condition of synthesis about 40 of colloid solution of Ag was obtained, differed in clarity and colors – from orange, through red, pink, violet, blue to green. The UV-Vis spectra of all of them were recorded to find out the position of the LSPR bands (Fig. 1). For the chosen 4 solution the TEM imagines were collected to get information about shape and size of nanoparticles. The shape distribution of shapes was calculated from amount of 250-550 number of nanoparticules for every of sample (Fig. 2). The general conclusion is that the amount of the small spherical NP is almost the same in every solution, the nanorods amount decrease and triangle and bigger circular and polygonal plates amount increase with LSPR band shifting to the higher nm. Some of this tendency seems to be a little broken in case of the two middle solutions, what is additional interesting effect.

3) <u>Check if SERS blinking is possible on them</u>

For SERS blinking experiments the sample was prepare as follow: on a clean glass drop of 0.1 ml anisotropic NP (blue) + 0.1 ml 3,3'-diethylthiacyanine iodine salt (λ_{max} 424 nm) dye was put and dried with compressed air duster, a drop of 1 M NaCl was dropped on this, and covered with another glass.

Before SERS blinking experiments also LSPR Dark Field images were collected for the prepared sample, which proved small contribution of scattering in the LSPR bands.

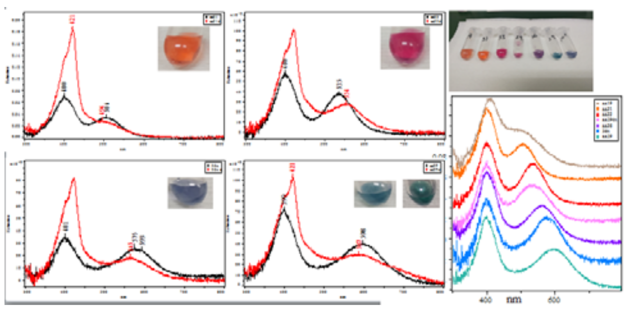

Fig. 1 UV-Vis spectra of chosen Ag NP solutions.

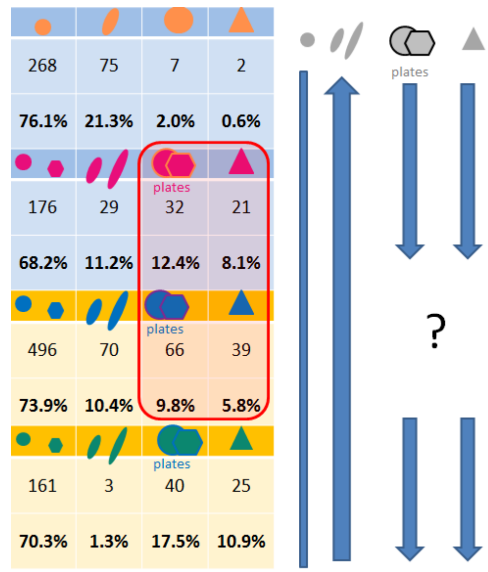

Fig. 2 Shape distribution of NP

As the SERS blinking turn out to be possible to observe, the complex of films has been recorded, differed in condition showed in the table:

resolution (ms)	duration (min)	amount
122	5	11*
122	5	16
61	5	10
61	10	7
61	20	13

*without drop of 1M NaCl

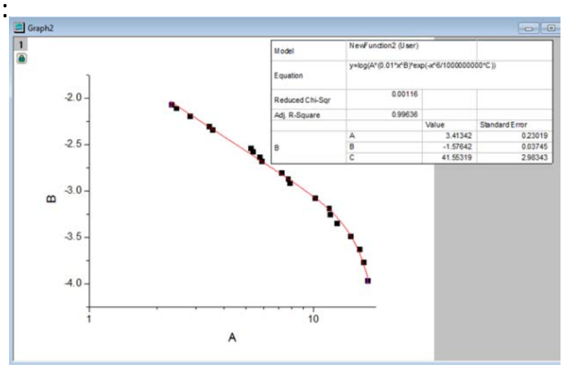

Fig. 3 Example for fitting the probability distribution in time with a new equation

After time profile analysis the set of data was collected – probability coefficient of bright and dark state and the truncation time for dark state were calculated, the histograms of its distribution are summarized and are ready to be compared with the results obtained for spherical nanoparticles by dr Kitahama.

During analysis of dark states of anisotropic NP different than for spherical NP dependents was observed. My proposition for a new analysis of SERS blinking equation is:

$$\log_{10}P_{off}(t) = \log_{10}(A_{off}t^{\alpha off}\exp(-t\text{^}\mathbf{D}/\tau))$$

The additional parameter D allow better curve fitting for different cases of anisotropic NP (Fig. 3).

The results obtained in this project will be described and published in international journal in cooperation with dr Yasutaka Kitahama and professor Yukihiro Ozaki.