focus

Single Molecule Activation and Computing

SEVENTH FRAMEWORK PROGRAMME

Work Package WP n. 9
High precision molecular activation by field enhanced two photon activation

Deliverable D9.2
Individually addressed molecular switches with AFM controlled interparticle gap.

Expected date: 17/04/2014

COLLABORATIVE PROJECT for

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Premise

The present Deliverable is associated with the task of **T9.2**, in which the aim is to address a molecular switch individually by the help of an AFM tip. In the deliverable list it was foreseen that addressing of a single molecule by making use of a metal nanoparticle attached AFM tip would be delivered. After an extensive amount of work it was shown in the second periodic report that the use of lateral space was not reliable and we have discarded that option to go for using the vertical space in order to construct the molecular gap. This technique is based on constructing a plasmonic dimer optical antenna by approaching a single nanoparticle attached AFM tip onto a periodic array of metal nanoparticles. In the first and second periodic reports we have shown that we were able to construct such a periodic metal nanoparticle array on a multitude of different substrate surfaces. Our efforts in the last period of the project on combining nanoparticle arrays with the nanoparticle attached AFM tip while sandwiching a fluorescent molecule were however hindered by the unexpected difficulties faced in constructing a reliable and useful metal nanoparticle attached AFM tip which could be used over and over again. In order to find a robust way of attaching a metal nanoparticle to the apex of an AFM tip we proposed to grow Si nanowires on the AFM cantilever in a metal nanoparticle assisted-growth mechanism. The preliminary results given in the second review report showed that this was possible, however, with a high density of wires grown on the entire surface of the AFM cantilever. Our efforts in the last period of the project on deterministically growing a single nanowire with a single metal nanoparticle at its apex turned out not to be a feasible option. During our extensive collaborative work that took place between METU and CBM in Ankara and Trieste, we however, were able to develop a very good theoretical understanding of second harmonic generation (SHG) from hybrid plasmonic-molecular systems. In fact, we have demonstrated that depending on the choice of parameters, SHG can both be achieved with a very high efficiency and be suppressed very strongly. Moreover, as a result of a very stimulating experiment, which was possible through an exchange stay of METU scientists at CBM, it was found out that efficiency of SHG can be boosted up to levels which enable direct observation of second harmonic light obtained from interaction of particular plasmonic system with continuous wave (cw) light source. This exciting new result is what we deliver for **D9.2** since we believe that providing a general understanding of SHG from plasmonic systems for the first time in literature and demonstration of super-high efficiency conversion of cw light is very illuminative.

Description of Work

A demonstration of deterministic construction of asymmetric metal nanostructures such as T-shaped, bow-tie or doubly-resonant plasmonic antennae for SHG were provided in the second report. Such structures are possible to construct by using E-beam lithography which limits the work space, is expensive and is a slow procedure. In this work we choose an alternate route for creating such asymmetric plasmonic structures on the large scale. We have achieved the task of fabricating SHG active asymmetric plasmonic structures by synthesizing Ag nanowires (AgNWs) using the polyol process (Coskun et al., 2011) and depositing them on transparent substrates by drop-casting. In a similar process involving different concentration of constituents, temperature and time, Ag nanoparticles (AgNPs) of a wide range of geometries are also obtained. The resulting AgNPs are co-deposited on the same transparent substrates. The result is a network of NW-NP complexes, which are ultimately asymmetric structures and cover a macroscopically large area. Such coated surfaces are first imaged by dark-field microscopy to ensure the existence of the complexes, and then mounted on our optical characterization set-up of inverted optical microscope – piezo-sample scanning stage combination. Initially the microscope's visual inspection camera image generated by halogen lamp illumination is used to find a candidate region of interest which potentially bears a NW-NP complex. After marking such a candidate location by the help of this image, the IR laser source and sample scan stage are activated for generating a monochromatic IR image in the back-reflection geometry. The samples are illuminated with cw IR laser source (1064 nm) using diffraction limited focal spot size of ~1 μm diameter. The Rayleigh back-scattered light of the same wavelength registered by a photodiode is used to generate a dark field reflection image by pixel-wise scanning of the sample in 2D. By the help of piezo-

stage, the illumination spot is placed at several locations along the axis of a single AgNW. At each spot, a spectrum is accumulated around the SHG wavelength of 532 nm. The resulting spectra are integrated and a SHG color map is produced.

Results and assessment

In order to ensure that we deposited the AgNW – Ag NP complexes, we have made darkfield optical images using a dark-field condenser in a dedicated microscope (**Figure D1**). Light colored long straight features in the image represent the AgNWs and the bright intense spots represent the AgNPs. The AgNPs are observed to display different colors such as green and blue under white light illumination as a result of their size dependent plasmon resonance in the visible range. The AgNWs are observed to show a reddish glimmer as a result of shift of their plasmon resonance towards IR due to high aspect ratio of their geometry. A combination of such two Ag nanostructures is what we expect to boost the SHG due to conversion of IR plasmons to visible plasmons upon interaction of NWs with NPs.

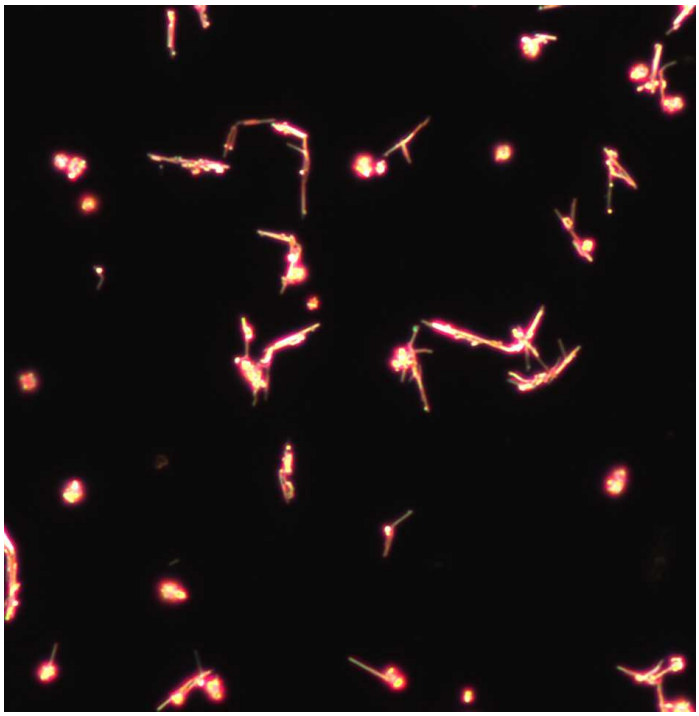
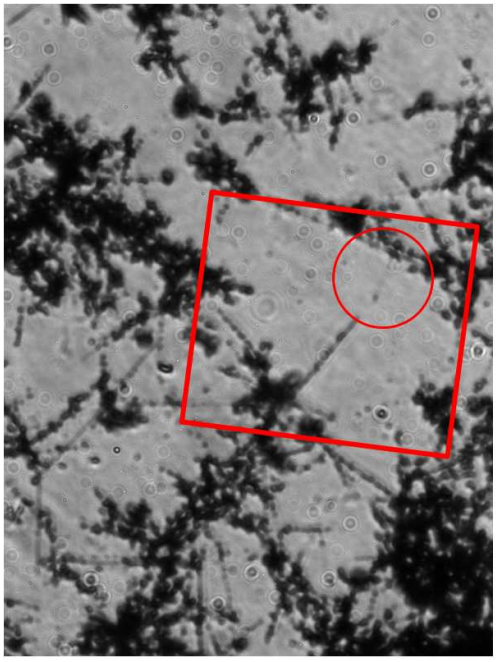
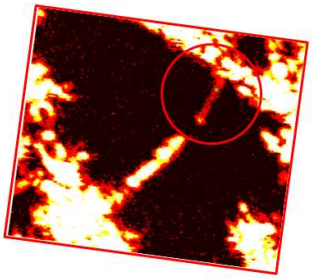


Figure D1: A darkfield image of the AgNW – AgNP network deposited on microscope cover-slip.

Next we place such a sample under our other optical setup (which is described in the previous project reports) with the piezo-stage. We first record a transmission image by the visual inspection camera that works in the visible. The dark figures in the image indicate the location of AgNWs, AgNPs and their clusters with a very poor resolution. Nevertheless this image is sufficient to locate a candidate region that bears a single AgNW-AgNP complex for further detailed study. The **Figure D2** shows such a transmission image. The red circle on the transmission image on the left points a region of possible interest with one NW and NP complex. The red rectangle indicates the region which is scanned at a high resolution by the piezo-stage. The reflection image produced by the scanning of the same region is given on the right using a 1064 nm IR laser. The reflection image produced at the illumination wavelength shows intense reflection from crowded clusters as well as a single straight feature which is the isolated part of a single AgNW and an AgNP attached towards the end of the AgNW. The faint straight shadow on the left image and a dark spot at its end appear as a straight bright feature on the left with a brighter spot at its end that indicates the attached AgNP.



Microscope Camera (Transmission)



Micro-Scan Image (Reflection)

Figure D2: A transmission image by the microscope camera on the left and a micro-scan reflection image of the area as indicated by the red rectangle, on the right. The red circles show a region with a single AgNW with a single AgNP attached close to its end.

Such AgNW-AgNP complexes are often encountered upon inspection of these samples with scanning electron microscope. **Figure D3** shows a zoomed version of the encircled straight part of the micro-scan image along with a representative sketch of the AgNW-AgNP complex drawn to scale. An SEM image is provided on the right that shows a highly magnified image of the end of AgNW with the attached AgNP along its body. The AgNW is typically of 50-60 nm in diameter and can be as long as 5-10 μm. The AgNPs are typically of 50-150 nm size.

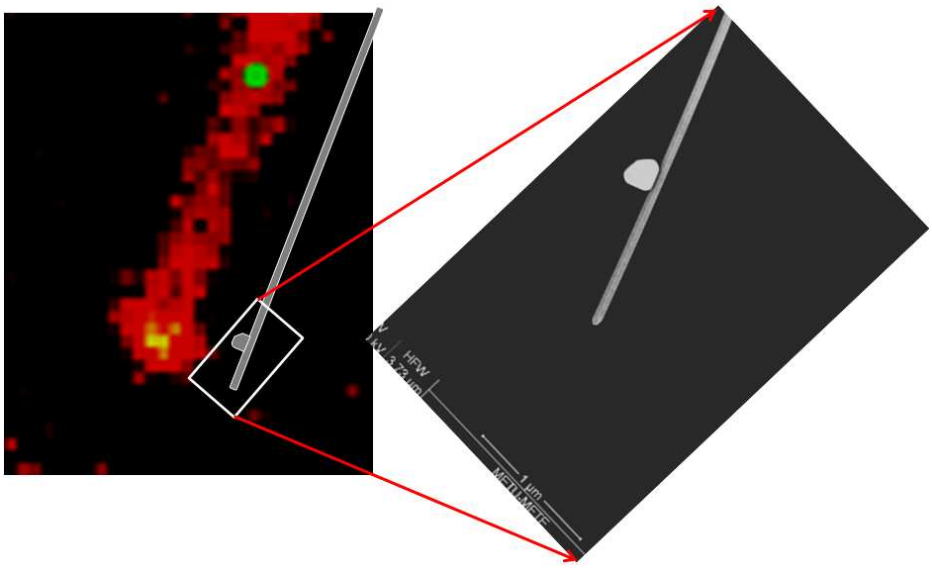


Figure D3: A zoom in into the encircled region in the micro-scan image along with a sketch of AgNW-AgNP complex. The SEM image on the right shows the end of the AgNW with high magnification.

The most important part of our work is detailed in **Figure D4**. By the help of the micro-scan image, we can direct our focal spot at any pixel of choice and acquire SHG spectra using a spectrometer – EMCCD combination (the green points in the image frames). In the figure we show a series of frames on which the particular choice of illumination spots are marked and at those positions SHG spectra around 532 nm of SHG wavelength are accumulated.

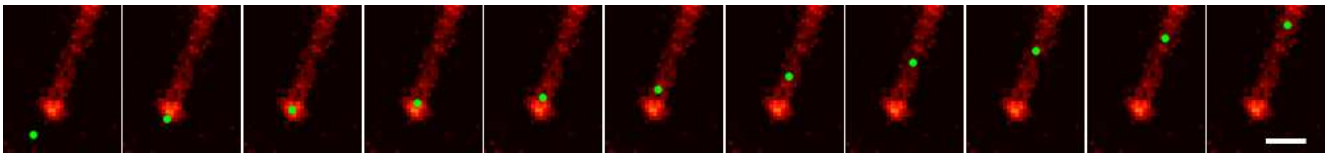


Figure D4: A series of IR micro-scan images with green markings showing selected illumination spots. The white scale bar represents 2 μm. The green points span a total of about 6 μm distance.

While moving the diffraction limited illumination spot along the axis of the AgNW, a SHG spectrum is acquired at each indicated green spot from left to right and the acquired spectra are plotted (**Figure D5** left panel). These spectra are integrated and the integral SHG signal is plotted against the distance along the AgNW axis (**Figure D5** right panel). There are 3 major results that we obtain. **1)** When the illumination spot is not located on the AgNW, no SHG signal is registered. So the SHG originates genuinely from the plasmonic structure. **2)** We observe SHG even with cw illumination (50 mW on the sample) from AgNW plasmonic structures. **3)** The SHG signal is enhanced by a factor of about 30 to 40 when the illumination spot is on the AnNP-AgNW complex with respect to the body of the AgNW alone.

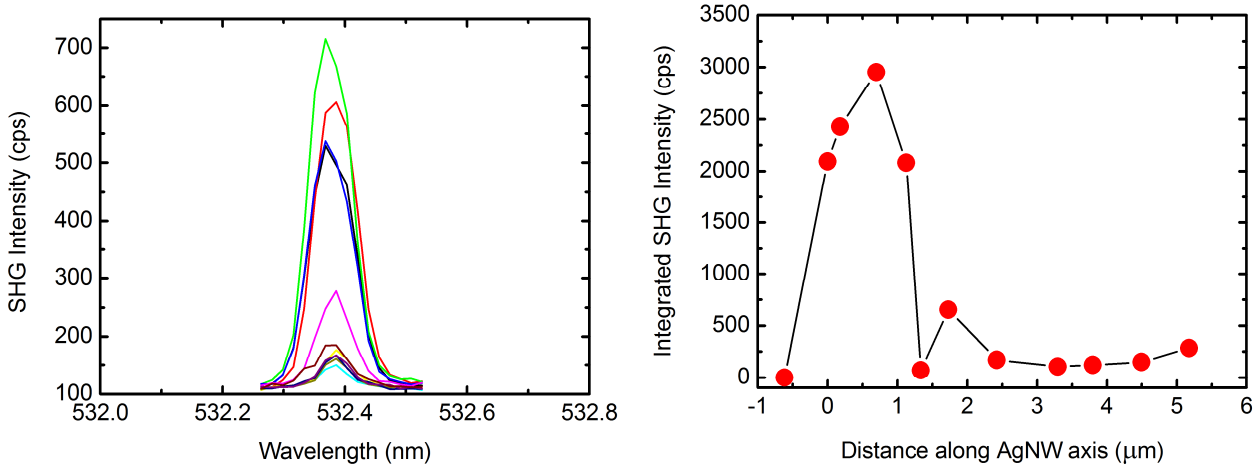


Figure D5: Left panel shows the SHG spectra obtained at different positions along the body of the AgNW, right panel shows the integrated SHG intensity as a function of position on the AgNW. In the right graph the breadth of the SHG signal peak along the AgNW axis is due to the 1 μm focal spot size.

A better visual represantation of the SHG intensity distribution as a function of position along the AgNW axis is given in **Figure D6**. A color bar is produced from the integral SHG signal and displayed in parallel with the actual SEM image and its representative straight extension. The SHG signal clearly starts to appear starting from the end of the AgNW and reaches its maximum around where the AgNP is attached to the AgNW. An overlap of the color bar with a represantation of such an AgNW-AgNP plasmonic hybrid complex on the right clearly depicts the observed effect: An effective SHG conversion spot is constructed by the hybridization of the AgNW and AgNP plasmons.

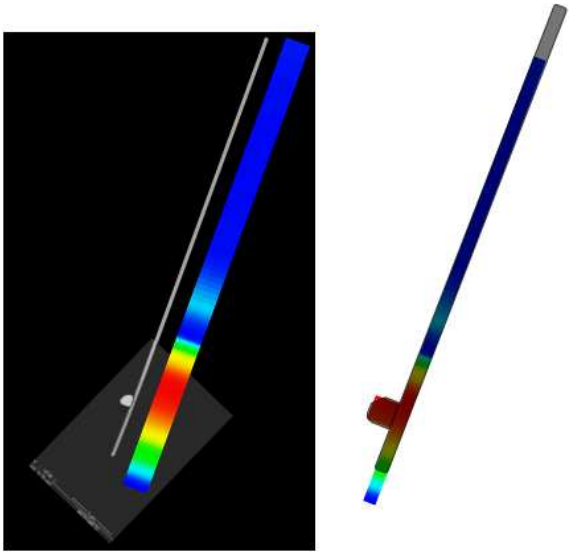


Figure D6: The SHG integral signal intensity as a color bar and the AgNW along with it, clearly show that the enhancement originates from coupling of the AgNW with the AgNP. The color bar superposed onto the represantative sketch of the system – on the right.

Our previous and present theoretical and expermental works on the subject (Tasgin, 2013; Turkpence, et al., 2013 and Salakhutdinov, 2014) proves that the dimensions of such a spot is as small as the contact area or the gap between the two different size (and even dimension) plasmonic nanostructures. Hence we can safely and clearly state that creation of a nanoscale light source by nonlinear optical activity of plasmonic nanostructures is delivered as a result of the present project.

Such a AgNW-AgNP complex can be fabricated such that the AgNP is attached closer to the end of the AgNW and therefore can be utilized as an efficient SHG center for adressing a single molecule on a surface when approached from the vertical space. However the use of vertical space depends strongly on the success
Along with the **D9.2** we hope to have demonstrated that the instrumentation for switching of single addressed molecule is fully developed conceptually, so that the **MS35** is attained, and also practically completed to the extend of the very last step in which actual attachment of the SHG system to an AFM tip apex was found not to be feasible, yet alternatively a dense arrangement of the demonstrated high efficiency SHG on a lateral surface cast itself as a feasible possibility.

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