Scientific report

1. Purpose of the visit;

The main purpose of this 9 week visit was to develop new research collaboration between Trinity College Dublin (Ireland) and Nanophotonics Group at Materials Physics Centre (MPC) in San Sebastian (Spain) in the area of plasmonic noble metal (Au/Ag) nanoparticles and J-aggregate dyes for photonic and sensing applications. We also aimed to use these studies to further develop our collaboration and apply for joint funding from EU FP7 and FP8 programmes.

2. Description of the work carried out during the visit;

The following research work has been carried out:

- We have synthesised and investigated by various instrumental techniques new silver and gold-coated silver nanoprisms and nanoboxes. In order to optimise the synthesis the influence of amounts of reagents on the morphology and size of metal nanostructures has been investigated in details.
- Pseudoisocyanine iodide, (PIC) J-aggregate dye has been incorporated into nanoboxes during the synthesis of nanoboxes, that resulted in new metal nanostructure- J aggregates.
- All nanomaterials and corresponding J-aggregate dye assemblies above have been investigated by a range of instrumental techniques. The photophysical properties of these materials have been investigated using UV-Vis and photoluminescence spectroscopy. The size distribution has studies by dynamic light scattering (DLS) and surface charge the nanostructures have been measured using ZetaSizer Nano. The morphology of the nanostructures was also studied by Transmission Electron Microscopy (TEM and HR TEM). The new nanomaterials have also been investigated by micro-photoluminescence setup and fluorescence lifetime imaging using experimental facilities of nanophotonics lab at MPC in collaboration with Prof. Yury Rakovich.

3. Description of the main results obtained;

3.1. Synthesis of new nanomaterials

A range of various silver nanoprisms were produced according to the previously reported by us procedure [1]. In the absence of trisodium citrate, gold was previously reported to grow towards the middle of the silver nanoprisms. Addition of a large amount of gold and ascorbic acid in excess thus showed to form a hollow triangular nanostructure which was designated as nanobox. Pseudoisocyanine iodide, (PIC) J-aggregate dye (10 nmol/L or 15 nmol/L) was added to 4mL of the suspension and the UV-Visible spectrum was recorded. Ascorbic acid (10mM, 0.5mL) and chloroauric acid (0.5 mM, 5mL, 12mL/hour) were subsequently added to form nanoboxes. The resulting nanomaterials were washed by centrifugation and re-suspended in water.

3.2 Characterisation and investigation of new nanostructures

Initial Au/Ag nanoboxes were characterised by a blue shift in the UV-Vis absorption spectrum compared to that of silver nanoprisms as shown on Figure 1; the shift increased with the thickness of the shell, which was found in published studies to be a gold/silver alloy.

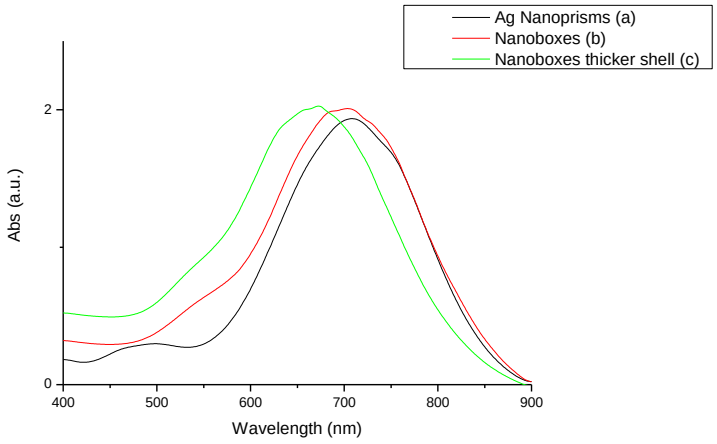


Figure 1: UV-Vis absorption spectra of silver nanoprisms and gold/silver nanoboxes

After the incorporation of PIC, a small peak appears when J-aggregates are formed upon contact with Ag nanoparticles. In contact with Au or Au/Ag nanoparticles however, J-aggregates are characterised by a dip in absorbance where the peak was before. The concentration of PIC greatly influenced the formation of nanoboxes, as seen from TEM and STEM images on Figure

2. At low PIC concentration the growth did not seem to be disturbed and the nanoboxes formed normally. As the concentration was increased, they became less regular. For concentrations higher than 15nmol/L they did no longer appear to be hollow. On the other hand, they clearly generated J-aggregates as showed in the UV-Visible absorption spectra in Figure 3. Importantly, the J-aggregate signal was not affected by washings which suggested that they were either strongly bound to the surface or trapped inside. As the PIC concentration was reduced to a level where the nanoboxes could form properly, any J-aggregate signal became too weak and was hindered by the plasmon peak. It should also be noted that the nanoprisms plasmon was overlapping the monomer and J-aggregate bands, making it difficult to ascertain the presence of J-aggregates. Luminescence of the samples and their lifetimes were also monitored with fluorescence confocal microscopy and FLIM (Figure 4) using experimental facilities in the nanophotonics lab at MPC. FLIM has clearly shown the presence of 2 life times (one short under 1 ns and one longer around 4 ns). In overall there was some increase in the life time of PIC in Au/Ag nanocomposites to compare with free dye.

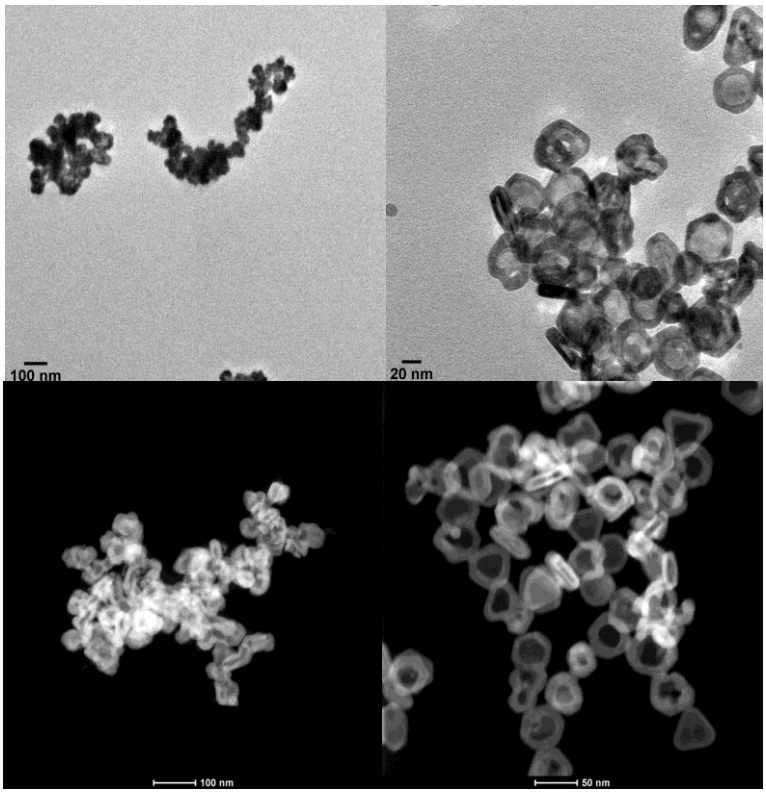


Figure 2. TEM and STEM images of Au/Ag nanoboxes formed in 15 and 10 nmol/L PIC respectively (left to right).

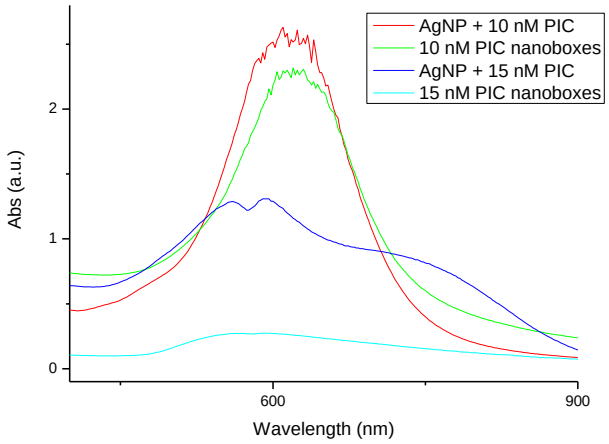
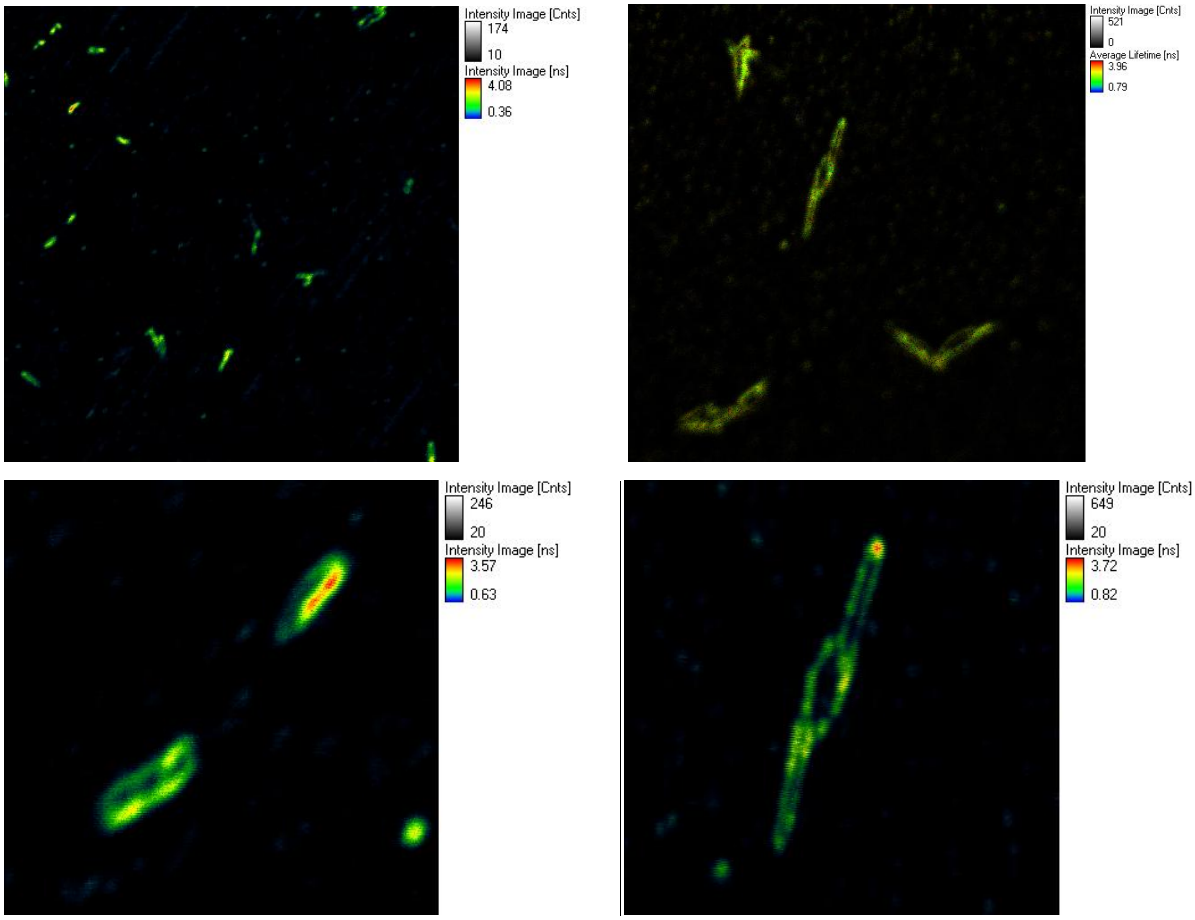


Figure 3 UV-Visible absorption spectra of silver nanoprisms and subsequently formed gold/silver nanoboxes in presence of 15 and 10nM PIC.



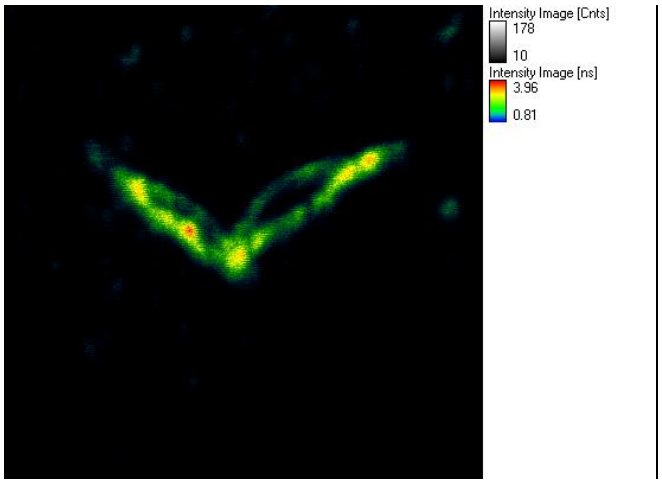


Figure 4. Photoluminescence intensity and lifetime images of Au/Ag nanoboxes with PIC J-aggregates.

[1] D. Aherne, M. Gara, J. M. Kelly, Y. K. Gun'ko, *Adv. Funct.Mater.*, 2010, **20** (8) 1329.

4. Future collaboration with host institution (if applicable);

We believe that these preliminary research studies are very promising and enable to develop a range of new plasmonic nanomaterials with a large number of potential applications. Our future work will involve photophysical studies of specific interactions between new nanostructures and selected biomolecules (e.g nucleic acids and proteins). Also, in order to get a dipper insight in the interaction of radiation and matter in developed hybrid nanomaterials theoretical investigation of local field distribution and optical response in Au/Ag nanoboxes are planned to be carried out. In the near future we plan to further develop this work and applications of the materials using funding from EU FP7 and FP8 programmes. In addition we will continue our collaboration on plasmonic nanostructures using ESF exchange schemes.

5. Projected publications / articles resulting or to result from the grant (ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant);

One manuscript on the preparation and studies of Au/Ag nanobox – J-aggregates ostructures are currently in preparation. We still need to complete some additional experimental studies and perform modelling of the system to finish our manuscript.

6. Other comments (if any).

I think that ESF Exchange Visit Grants are very useful and provide an excellent value for money. I hope that this scheme will be continued in the future.