Development of new chiral sensors using anisotropic plasmonic nanomaterials

1. Purpose of the visit

The main purpose of the visit was to continue the research collaboration between Trinity College Dublin (Ireland) and Prof. Yury Rakovich and Nanophotonics Group at Materials Physics Centre (MPC) in San Sebastian (Spain) in the area of plasmonic noble metal nanomaterials for sensing applications. This project was is develop and test anisotropic 1D plasmonic nanostructures for chiral sensing of single enantiomeric molecules such as DNA and selected important chiral drugs. In our original submission we have asked for 12 weeks project, but only 4 weeks project was granted therefore we were not able to perform all experiments which we have planned initially. However, we have developed new interesting direction in optically active plasmonic nanomaterials.

2. Description of the work carried out during the visit

The work have involved following stages:

(i) The synthesis of silver (Ag) nanowires of controlled diameter and length;

(ii) Investigation of optical properties of Ag nanowires using various spectroscopic techniques;

(iii) Investigation of the origin of CD signal in Ag nanowire suspensions

(iv) photophysical studies of specific interactions of 1 D plasmonic nanostructures with selected chiral luminescent compounds using UV-Vis, CD and micro-photoluminescence setup and fluorescence lifetime imaging.

3. Description of the main results obtained

3.1. Synthesis of nanowires

Initially we have synthesised silver nanowires of controlled length and diameter using slightly modified previously reported procedure [1]. Briefly, a mixture of 0.334 g PVP (polyvinylpyrrolidone) and 20 mL of ethylene glycol was heated and thermally stabilized at 170 °C in a flask. Once the temperature has been stabilized, 0.025 g of silver chloride (AgCl) is ground finely and added to the flask for initial nucleation of the silver seeds. After three minutes, 0.110 g of silver nitrate ($AgNO_3$), the actual silver source, is titrated for 10 min. After that, the flask was heated for an additional 30 min to ensure that the growth is complete. The cooled-down solution is then centrifuged three times at 6000 rpm for 30 min to remove solvent (EG), PVP, and other impurities in the supernatant. After the final centrifuge, the precipitate of Ag NWs were redispersed in 30 mL of water.

3.2. Investigation of optical properties of Ag nanowires

During our first CD characterisation experiments we have found that silver nanowires on their own demonstrate quite strong CD response (Figure 1) without having any chiral species around. We decided investigate this phenomenon in details.

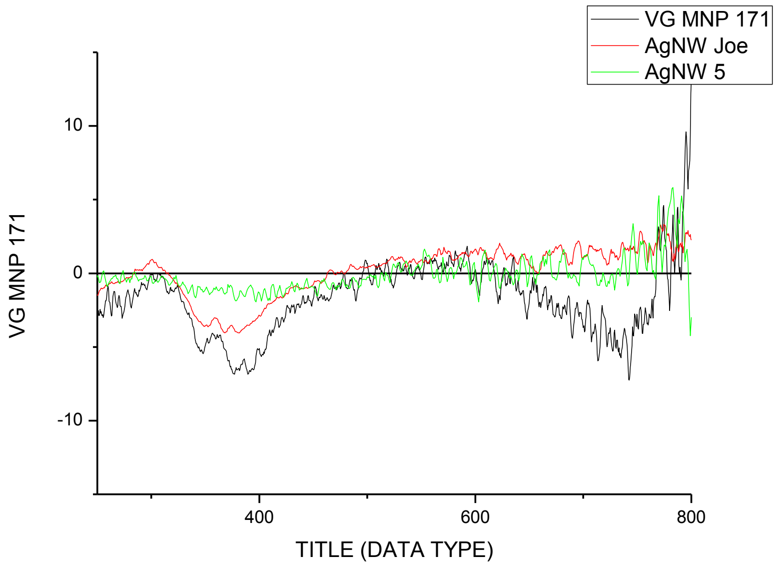

Figure 1: CD spectra of Ag nanowire samples from various syntheses and batches.

We have performed CD spectroscopy and TEM monitoring of Ag nanowires. This was achieved by taking probes at different stages of the synthesis and by performing TEM imaging and CD spectroscopy of selected probes. These results are summarised in Figure 2. It is clear that strong CD signals appear only after the formation of 1D Ag nanostructures. Thus we can conclude the Ag nanowires are optically active and can demonstrate circular dichroism without having any chiral species around. Initially it was hard to understand the real reasons of that. However, during one of the experiments we have found that CD signal in nanowire suspension can be induced and controlled by a simple vortex (stirring the solution and suspension in the cuvette). By stirring the solution in cuvette clock- and anticlock- wise we can produce mirror image CD signals (Figure 3). This was only observed for silver nanowires, nothing like that was seen for silver nanoparticles or small metal nanorods. Moreover, we have found that the residual

CD signal in the cuvette remains even if we leave the cuvette standing still for 1 hour in our CD spectrometer.

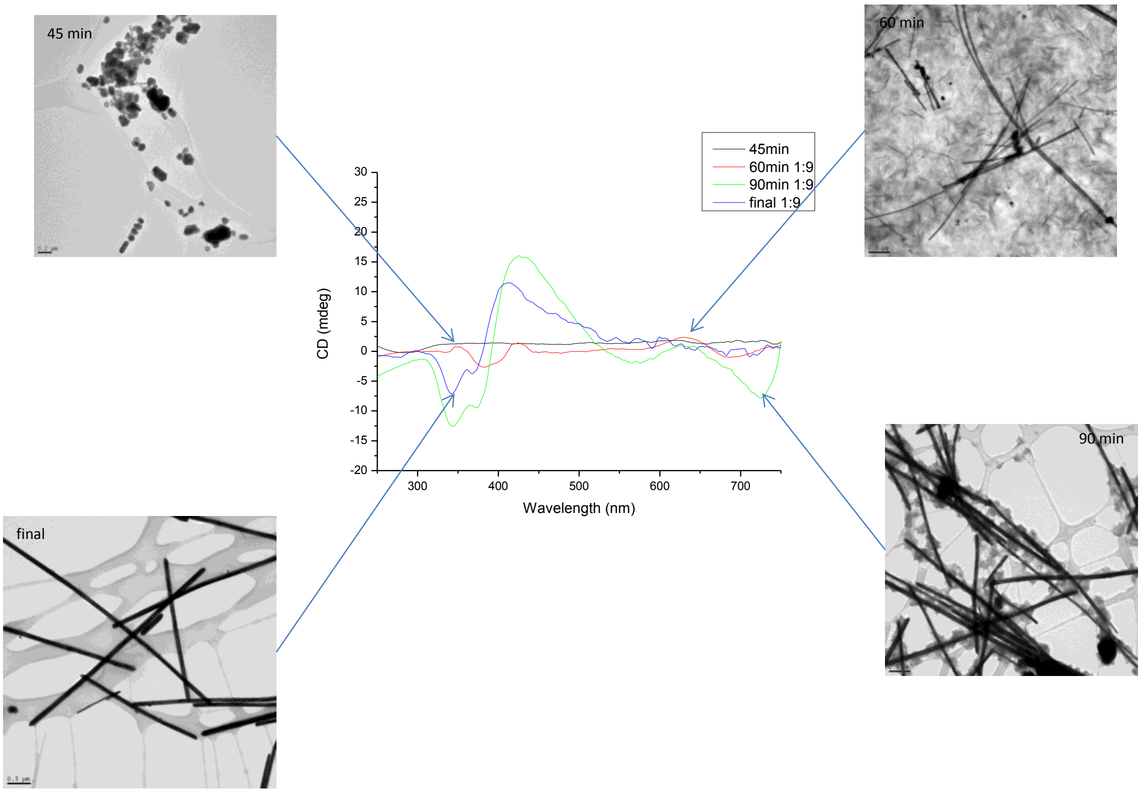

Figure 2: Dependence of CD response from the size and shape of plasmonic Ag nanostructures.

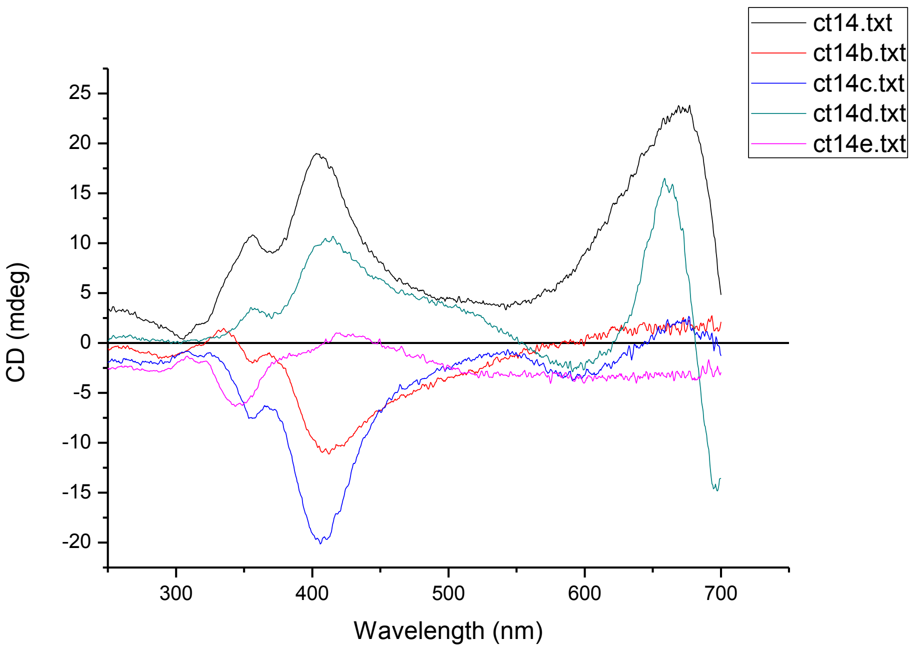

Figure 3: CD spectra of silver nanowires left to settle in the CD machine (a-c) followed by re-shaking (d) and then settling again (e).

In addition, we have found that CD signal remains in the solid samples. For example if we drop the sample of nanowires on the quartz slide and slightly stirring the solution clock- and anticlock- wise before drying we can produce mirror image CD signals (Figure 4).

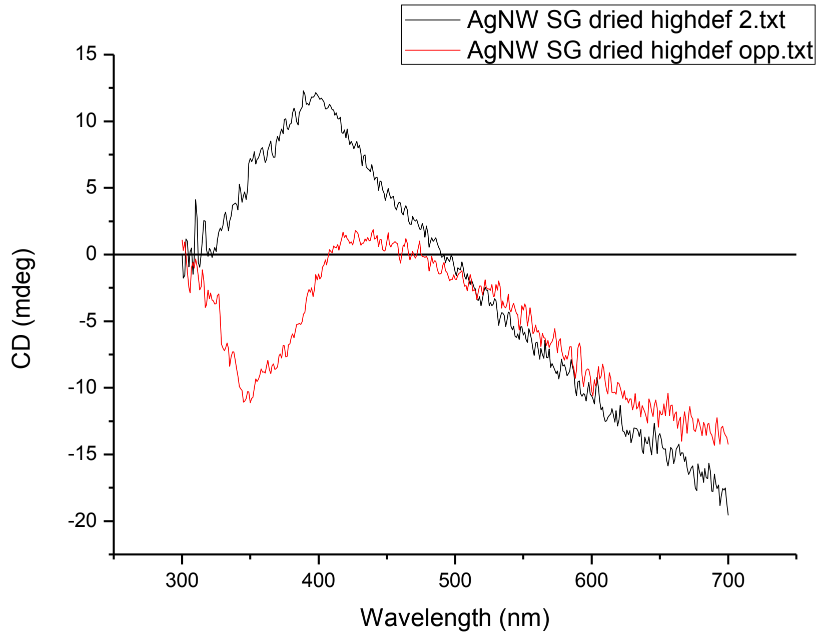

Figure 4: CD scans of dry silver nanowires stirred in opposite direction on the quartz slide.

We have also performed FLIM imaging of these nanowires on the quartz slides. To achieve the better FLIM contrast our silver wires were blended Rhodamine 6G and Pseudoisocyanine iodide (PIC) J-aggregate dyes (Figure 5 below). We expect that this structures should emit circular polarised light, but unfortunately we had no appropriate machine and time to perform circular polarised light emission of these materials. This will be subject of our future work and collaboration.

References

Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. Crystalline Silver, Nanowires by Soft Solution Processing. *Nano Lett.* **2002**, *2*, 165.

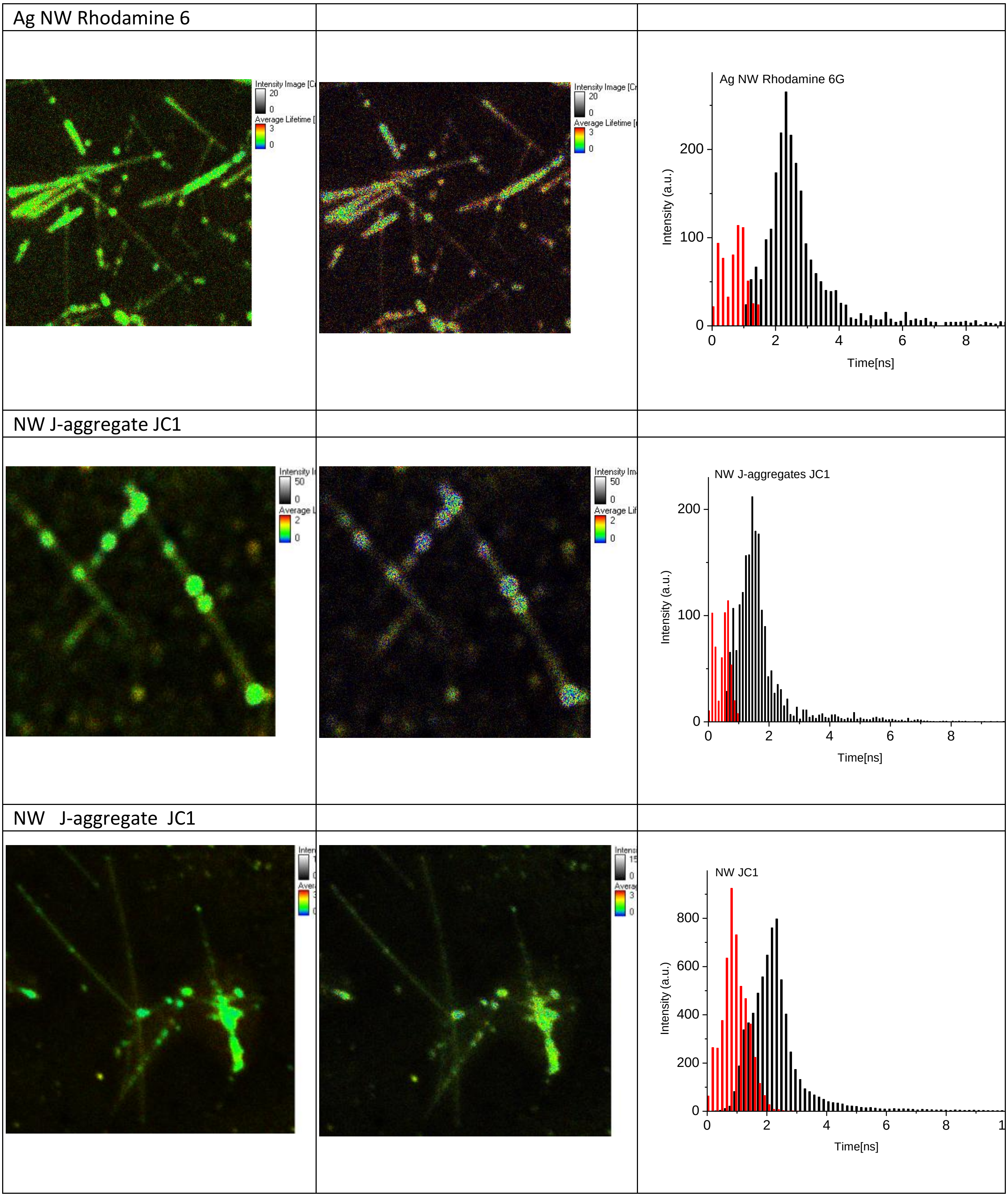

Figure 5: FLIM imaging of Ag nanowires deposited with Rhodamine 6G and Pseudoisocyanine iodide (PIC) J-aggregate dyes on quartz slides.

4. Future collaboration with host institution (if applicable)

As mentioned above we plan to continue our collaboration with Nanophotonics Group at Materials Physics Centre (MPC) and study the phenomena demonstrated by silver nanowires and corresponding plasmonic nanostructures in details. Our future research will involve detailed studies of the long term retention of CD signal in suspension of silver nanowires and circular dichroism from structures of silver nanowires which are deposited on solid substrates. We also plan to use the silver nanowires and corresponding optically active structures above for chiral (CD) sensing of single enantiomeric molecules such as DNA and selected important chiral luminescent drugs (e.g. ibuprofen, naproxen, moxalactam, warfarin). In the near future we plan to further develop this work and applications of the materials using funding from Horizon 2020 programmes. In addition we hope to 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)

We have started the preparation of the manuscript on the circular dichroism phenomena in Ag nanowires and corresponding structures. However, we still need to complete some additional experimental studies and possibly perform computer modelling of the system to finish our work and write a good quality manuscript.

6. Other comments (if any)

I think that ESF Exchange Visit Grants are very useful. I do not know any other grant scheme which could provide such good value for money. I hope that this scheme will be continued in the future.