Scientific Report

PLASMON - Short Visit Grant – 4436

“Nonlinear optical properties of hybrid system of plasmonic nanoparticles and J-aggregates”

1. **Purpose of the visit**

The aim of this visit was to establish research collaboration between Nanophotonics Group at Materials Physics Center (Donostia-San Sebastian, Spain) and Semiconductor Photonics Group at Trinity College (Dublin, Ireland) leading by Prof. John Donegan.

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

During this visit we investigated nonlinear optical properties of hybrid system consisting of silver and cupper nanoparticles and nanowires and cyanine dyes in J-aggregate state using femto-second z-scan facilities at Trinity College.

3. **Description of the main results obtained**

The main result is observation of enhancement of nonlinear refraction in hybrid system.

Z-scan technique was performed by sending an axially symmetric converging beam through the hybrid sample that was placed near the beam waist (Fig.1).

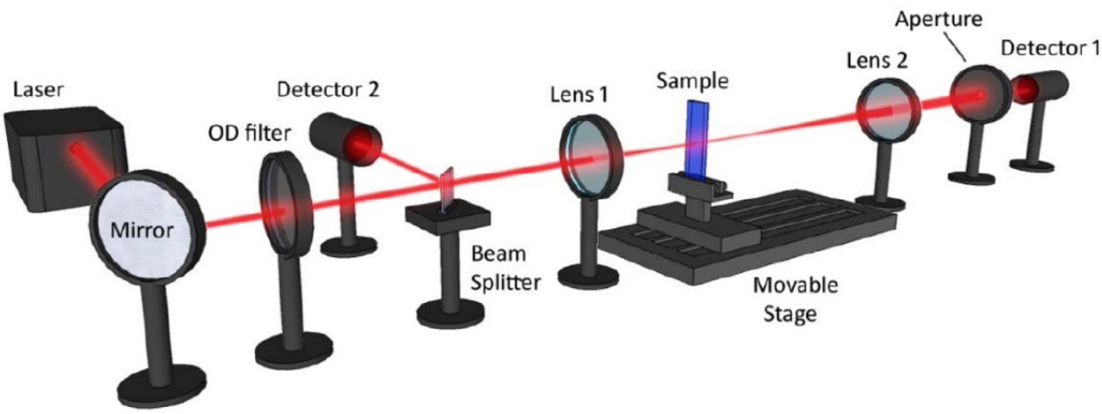


Figure 1. A Z-scan set-up. The intensity of the laser is adjusted with OD filter. The beam splitter separates the laser beam into reference and main beams. The reference signal is measured by Detector 2, and is used to correct the data for laser intensity fluctuations. The main beam is focused by Lens 1 and is later collimated by Lens 2, before passing through an aperture in the far-field. The sample is moved along the optical path of the focused measurements beam (Z direction), and the transmittance changes due to the sample are measured by Detector 1.

Z-scan measurements were performed using a LTS150 motorised stage (ThorLabs). The laser beam was focused and collimated by bi-convex spherical lenses (ThorLabs). The wavelength of the pulsed laser beam from a Verdi V10 laser (<130 fs, 80 MHz, Coherent) was set to 1.4 μm using the Mira 900/Mira-OPO system (Coherent). The intensity of the incident beam was adjusted using a series of neutral density filters (NT59 series, Edmund Optics). The intensities of the reference beam and the transmitted measurement beam were measured using two silicon photodiodes (SM05PD1B, ThorLabs) amplified by two photodiode amplifiers (PDA200C, ThorLabs). These intensities were recorded as a function of sample position using a LabView program that incorporated the ThorLabs software for the motorised stage. The measured transmitted intensity was first corrected for laser fluctuations by dividing it by the intensity of the reference beam. After being normalized to transmission at the Z=0 position, the corrected Z-scan trace was fitted to equation (1) to extract the values of phase changes due to the nonlinear absorption and nonlinear refraction.

$$T(x) = 1 + \frac{2(-\rho x^2 + 2x - 3\rho)}{(x^2+9)(x^2+1)} \Delta\Phi_0 \tag{1}$$

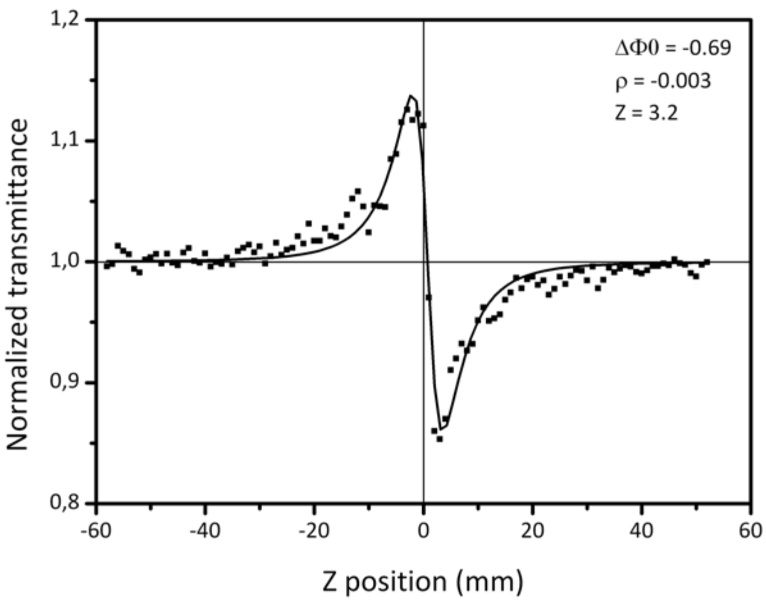
Here, $x = Z/Z_0$ where Z is the position of the sample relative to focal plane and Z_0 is the diffraction length of the focused beam ($= k(w_0)^2/2$), where $k = 2\pi/\lambda$ is the wavevector and w_0 is the radius of the beam waist. ρ is a parameter that relates the phase changes caused by non-linear absorption ($\Delta\Psi_0$) and nonlinear refraction ($\Delta\Phi_0$) or, equivalently, the nonlinear absorption and nonlinear refraction n_2 indices:

$$\rho = \frac{\Delta\Psi_0}{\Delta\Phi_0} = \frac{\beta}{2k\, n_2} \tag{2}$$

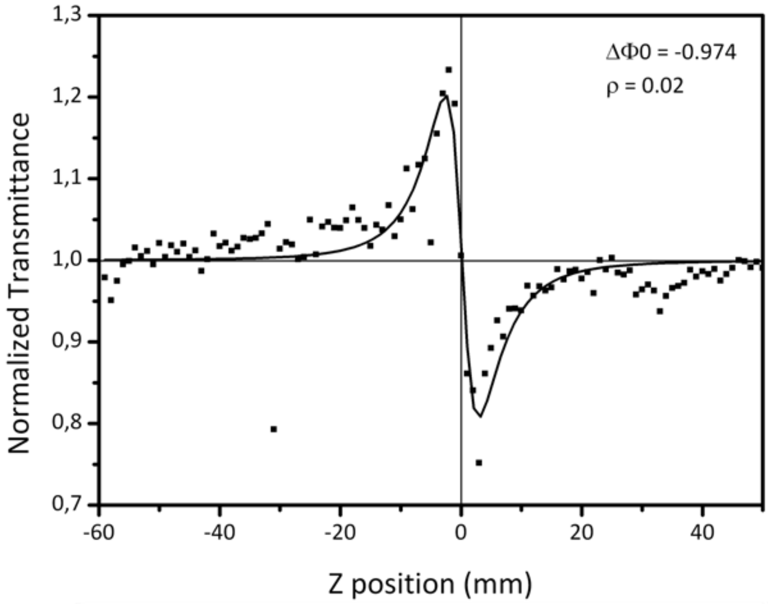
The hypothesis that the enhancement of the nonlinear properties of J-aggregates can be caused by the presence of metal nanowires and nanoparticles was tested on three hybrid samples assembled from 1,1′-Diethyl-2,2′-cyanine iodide (PIC), colloidal silver nanoparticles of ~30 nm average size (sample 1), silver nanowires of ~80 nm diameter (sample 2) and cooper nanowires of ~100 nm diameter (sample 3).

The results of z-scan measurements are presented in Figure 2.

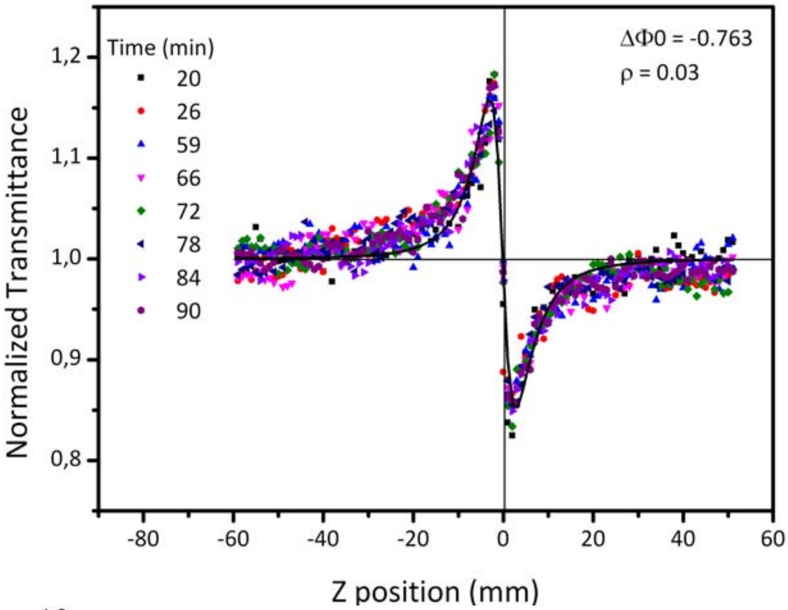
a)



b)


ΔΦ0 = -0.974
ρ = 0.02
Normalized Transmittance
Z position (mm)

c)


Time (min)
20
26
59
66
72
78
84
90
ΔΦ0 = -0.763
ρ = 0.03
Normalized Transmittance
Z position (mm)

d)

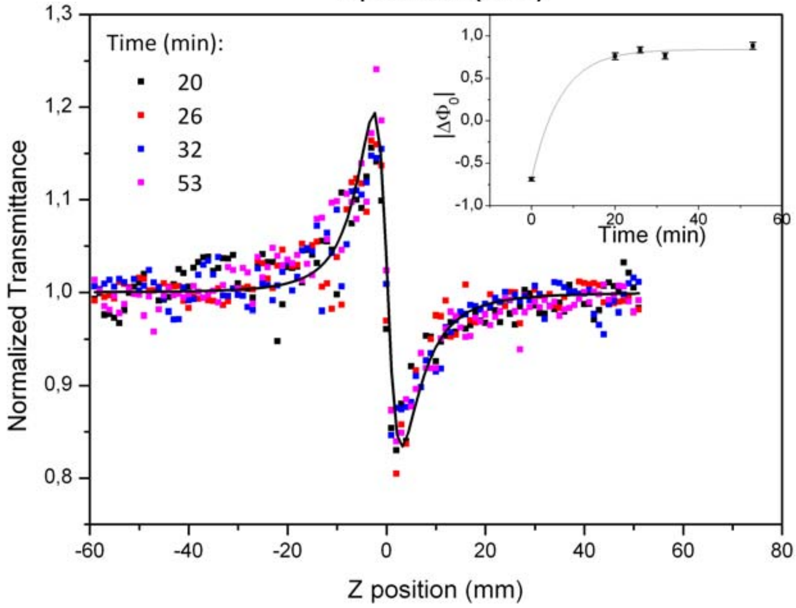

Time (min):
20
26
32
53
|ΔΦ0|
Time (min)
Normalized Transmittance
Z position (mm)

Figure 2. Z-scans of aqueous solutions of J-aggregated PIC (a), sample 1 (b), sample 2(c) and sample 3(d).

The values of $\Delta\Phi_0$ estimated from these z-scan curves were significantly larger for hybrid metal complexes assembled with the J-aggregates than $\Delta\Phi_0$ value of J-aggregates alone (Figure 3).

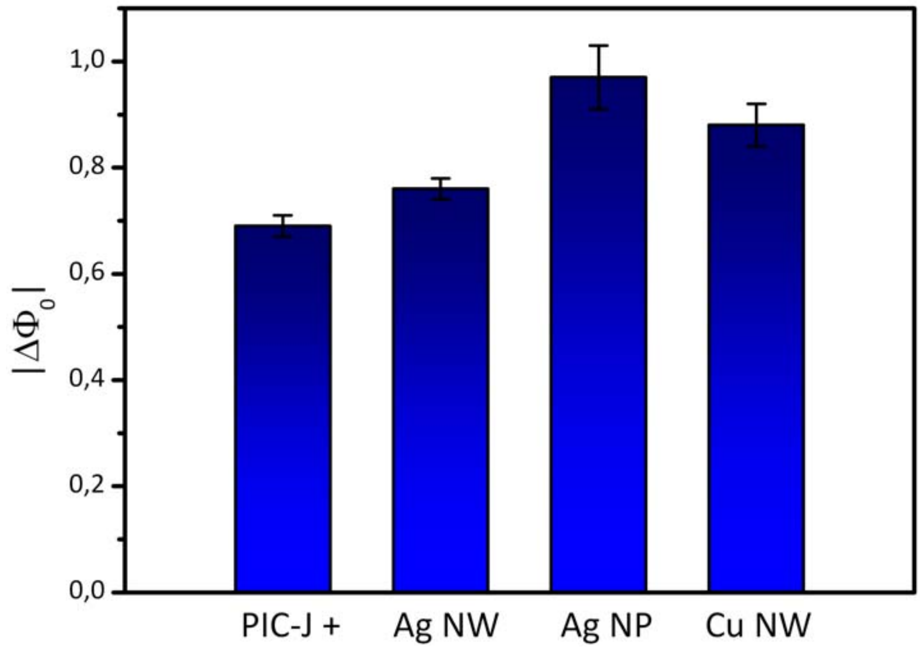


Figure 3. The absolute values of $\Delta\Phi_0$ for all samples studied.

We also observed strong growth of $\Delta\Phi_0$value with time for samples 2 and 3 (Fig. 2 (c) and (d), respectively). The origin of this effect is not well understood yet and has to be further investigated.

4. Future collaboration with host institution

This feasibility study allows us to build stronger collaboration between involved research groups for further development of new advanced materials for sensing and other photonics applications. As the next step extra research work is required to explain effect of strong growth and saturation of value of nonlinear refraction with time. Also wavelength-dependant Z-scan measurements can provide dipper insight into mechanism of plasmon-enhanced nonlinear properties of hybrid materials.

5. Projected publications

We plan to report main results of this work in paper invited for publication in “Colloidal Nanoplasmonics” special issue in Langmuir early next year. EFS support will be acknowledged.