Heat-enhanced plasmon driven coupling reactions

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The strong interaction between plasmonic nanoparticles and light has opened a new perspective of driving chemical transformation on nanoparticle surfaces. These chemical transformations could be initiated by charge/carrier transfer between the metal and the adsorbate or by plasmonic heating of the nanoparticle.[1] Plasmon-driven dimerization of 4-nitrothiophenol (4-NTP) into 4,4'-dimercaptoazobenzene (DMAB) on gold nanoflowers and the kinetics of the reaction were investigated by time dependent-surface enhanced Raman scattering (SERS).

Fig. 1 shows time dependent SERS spectra of 4-NTP adsorbed on gold nanoflowers. It can be seen that the Raman peak at 1332 cm^{-1} which is assigned to the NO_2 stretching mode decreases with time. Meanwhile, three new peaks appear at 1134, 1387, and 1434 $cm^{-1}$and their intensities increase with the irradiation time which can be assigned to DMAB vibrational modes.[2]

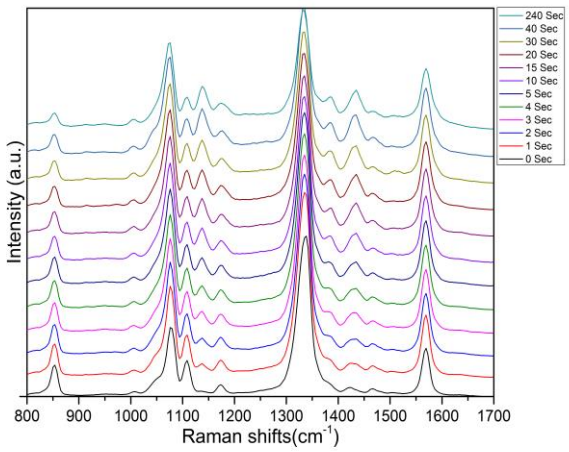

Figure 1. Time dependent SERS of 4-NTP

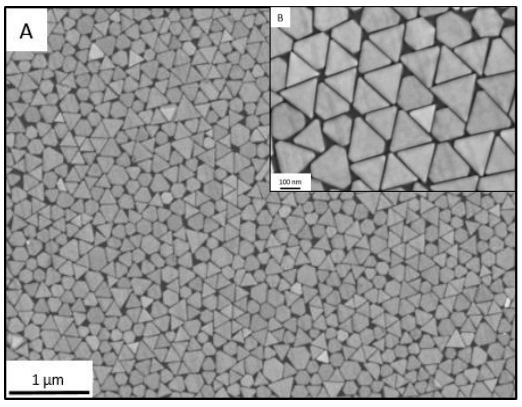

Figure 2. a) SEM image of large scale gold nanotriangles used in X-ray experiment, b) inset of well alligned gold nanotriangles on Si substrate.

The kinetics of the photo-dimerization process were studied under different conditions. The rate of the reaction was found to increase with increasing the laser intensity at constant temperature. Furthermore, the rate of the reaction increases with increasing the operating temperature under constant laser intensity. However, the reaction did not proceed under heating without light irradiation or without gold nanoparticles. This suggests that the reaction is initiated by optically triggered charge transfer from the metal nanoparticles and thermally activated by the heat deposited by the laser. Hence, X-ray measurements of the particle temperature were employed on large scale monolayer of gold nanotriangles (shown in Fig. 2) during irradiation with a CW laser. The measurements show that the particle temperature increases during the photo-reaction confirming the role of laser-induced heating.

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References:

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