Dye-Coated Nanoparticles: Two-photon Absorption and Time-Resolved Spectroscopy of Silver Nanoparticles Coated with D-π-D Nonlinear Optical Chromophores

Scientist at Georgia Inst. of Tech., Massachusetts Inst. of Tech., and at Wayne State Univ. are exploring the possibility of enhancing the two-photon cross-sections as well as the emission of organic chromophores by assembling them on silver metal nanoparticles. Error! Not a valid link.

Organic chromophore-metal nanoparticle assemblies have been synthesized and characterized in order to probe the organic-metal surface plasmon interaction. In particular, Silver (Ag) metal nanoparticles with two-photon absorbing chromophores assembled on to the particles in a tight packing order were synthesized. (**Marder, Perry, Ga. Tech.**) Characterization of the materials suggested that a relatively large number of chromophores were attached to each particle. Scanning probe microscopy of the self-assembled system was carried out (**Stellacci, MIT**). Distinct domains (ridges) were observed which suggest some degree of order in these metal-chromophore hybrid structures. A paper on this novel phenomenon was published two months ago in Nature Materials. Other authors of the paper were Alicia Jackson, a graduate student, and Jackob Myerson an undergraduate student Two-photon absorption (TPA) cross-sections were investigated (**Perry, Ga. Tech.**) for the nanoparticle assemblies as well as for the free chromophore in solution. A large cross-section was obtained for the nanoparticle assemblies (1.6×10^6 GM) with fs laser pulses. The effect of the interaction with the metal nanoparticle on the chromophore transition was not strong. Also, in consideration of the very large number of chromophores, one might expect a strong interaction among closely spaced (packed) chromophores. From the TPA results it appears that the chromophores may be only weakly interacting. Time resolved fluorescence anisotropy measurements were carried out as well with the chromophore-metal particle assemblies (**Goodson, WSU**) and a fast anisotropy decay process was observed which decayed to a relatively high residual value (~0.15). Transient absorption anisotropy measurements were also carried out and again a fast anisotropy process was observed which decayed to a larger residual value (0.2) than what is expected (0.0). The significance of the fast decay and larger residual value than is expected is is likely associated with the fast energy migration of the excitation among the chromophores on the roughly spherical Ag particles. The fast anisotropy decay suggests there is some fast orientational or energy transfer process in the system. However, the relatively large residual anisotropy suggests that a sizable degree of polarization is retained for long times. This may indicate the formation of somewhat ordered domains wherein the transition dipoles have a sizable order parameter, or relatively small regions wherein chromophore interactions are significant in the shell on the surface of the nanoparticles. These nanoparticle-chromophore systems provide an interesting arena for studying intermolecular interaction in constrained geometries and may be useful in application areas of photo-delivery mechanisms and TPA imaging.

The NIRT program at WSU has been able to attract summer students from a variety of backgrounds. In collaboration with the ACS project SEED program, summer students from Detroit Public Schools have carried out research projects related to the fabrication of metal nanoparticle architectures, and have characterized these systems utilizing laser spectroscopy. Working with both talented graduate students and postdoctoral fellows, summer students have been able to learn and gain experience about the basics of the chemical characterization as well as in steady-state and time-resolve fluorescence measurements of novel materials. Goodson has also taught a graduate course in spectroscopy of novel materials (such as the kind in this highlight). Stellacci has developed a new course for undergraduates called “Nanoscale Materials” in which he teaches about nanoparticles, nanowires and nanotubes.