Linear and nonlinear optical effects in hybrid self-assembled layers of nanoparticles

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Abstract-We show that hybrid nano materials composed of several different types of nanoparticles show exciting new linear and nonlinear optical effects. Furthermore, we will address the role of chiral inclusions in these layers on the optical properties.

While individual nanoparticles (NPs) can show interesting optical effects, it is often desired to organize these nanoparticles in layers to create nanostructures materials. This is usually done by Layer-by-Layer (LbL) self-assembly deposition methods that offer an attractive way to produce such structures in a very controllable way. Most of these LbL methods involve the use of polymers or polyelectrolytes as spacer and stabilizing unit between consecutive NP layers. Disadvantages of such methods are that they typically have limited NP filling/volume fractions. (1)

Recently, we developed a versatile LbL fabrication method on glass substrates using short bifunctional molecular linkers that results in homogeneous samples with very high NP filling fractions and controlled distances between adjacent particles. This synthesis method uses short bifunctional molecular linkers connecting the NPs and allows producing nanocomposites with a defined number of NP layers of specific materials on glass substrates. (2)

One concrete type of samples that we prepared are composed of alternating layers of silver NPs, Fe$_3$O$_4$ NPs and gold NPs. The resulting structures show a variety of optical resonances in the visible and near-infrared region of the spectrum and exhibit peculiar linear and nonlinear optical properties. For example, nanolayered structures deposited on one side of the glass substrate show nonreciprocal asymmetric transmission effects on the order of 0.1%. Furthermore, the effect is additive, in the sense that asymmetric transmission increases linearly with the number of samples put into a consecutive assembly. The origin of the asymmetric transmission effects is twofold: 1) the presence of a strong asymmetry perpendicular to the sample created by using different types of NPs, and 2) the presence of strong quadrupolar interactions between the different particles. The corresponding dielectric tensor can be shown to be different for the forward and backward propagation direction leading to a truly nonreciprocal effect. We will present a relatively simple theory based on electric-quadrupole effects, that explains all experimentally observed effects.

The same type of sample was used to examine second-harmonic generation (SHG) and third-harmonic generation (THG). While not a classical nonlinear optical material, both second-harmonic and third-harmonic efficiencies of the samples are extremely strong. Especially the third-order response is extremely high, amounting to susceptibility values of over $10^{-10}$ esu. Furthermore, spectrally resolved nonlinear optical measurements under variable NIR excitation wavelength show that at particular excitation wavelengths, both SHG and THG become simultaneously resonantly enhanced. We show that SHG is enhanced due the the presence of strongly coupled plasmon fields, while THG is enhanced due to strong IVCT transitions in the iron oxide NPs.
Finally, the NP multilayeres were doped with chiral molecules and circular-difference (CD) effects in the optical response were investigated. Strong CD effects were observed, depending on the particular experimental configuration.

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REFERENCES