Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Shell-thickness-dependent nonlinear optical properties of colloidal gold nanoshells

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SUPPORTING INFORMATION

1. Example of the determination of the wavelength dependence of nonlinear refraction contributed by the nanoshells

The nonlinear refraction was determined directly from CA scans taken for all the samples as well as for cells with solvent only, as values of n_2. Such data are quantities which are not characteristic for the nanostructures, they are values for solutions of given concentrations, not very different in value from those for the solvent alone, typically on the order of 10^{-15} cm^2/W (that is, the contribution of the nanoshells to the value of n_2 may be relatively small due to their low concentration). Therefore, quoting n_2 values (or rather presenting n_2 spectra) is of little significance for comparisons with data on other systems.

The proper way of presenting the nonlinear refractive contributions of the nanoshells is giving a microscopic quantity which is responsible for their contribution to n_2. In the simple oriented gas approach this is done by assuming the Lorentz local field factors and calculating the real part of the cubic hyperpolarizability $\gamma\ (-\omega;\omega,-\omega,\omega)$.

Such values are given below as the spectrum of the hyperpolarizability vs wavelength for sample "NSs 1" (Fig. S1).

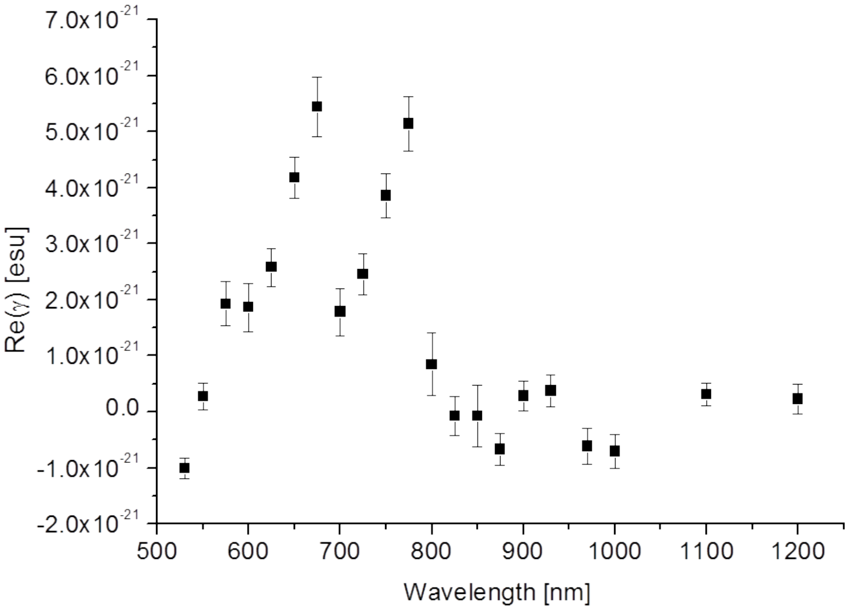

Fig. S1 Dispersion of the real part of the complex hyperpolarizability γ for "NSs 1"

Notable are relatively high, positive values of Re(γ) in the range of wavelengths corresponding to both the one-photon absorption band of the nanoshells and the range where strong one-photon saturation is observed. This is no surprise, since, through Kramers-Kronig type relations, any modification of one-photon absorption strength, formally treated as a higher-order term in the expansion of the absorption coefficient vs. intensity results also in the change of the refractive index, again, formally equivalent to appearance of contribution to n_2. However, it must be kept in mind, that treating absorption saturation as simply a negative nonlinear absorption coefficient is a very crude approximation and, in a similar way, treating the changes in the refractive index due to the saturation as a cubic nonlinear phenomenon is incorrect, too. Thus, the data shown here can only be treated as effective values, having the character of illustration of consequences of the complex interplay of absorption saturation with other nonlinear phenomena.

2. Examples of open- and close- Z-scans curves for silica, solvent and uncoated silica nanospheres performed at 530 nm.

The measurements of Z-scans for suspensions of uncoated silica spheres were performed at approximately the same number density as that used for the other nanoparticles (this amounted to 0.05 mg/ml). The wavelengths used were 530, 550, 575 and 600 nm. In all cases the CA curves were identical to those obtained for the pure solvent and the OA curves showed no indication of any nonlinear absorption (or nonlinear scattering) process. Fig.S2 shows example of results obtained at 530 nm.

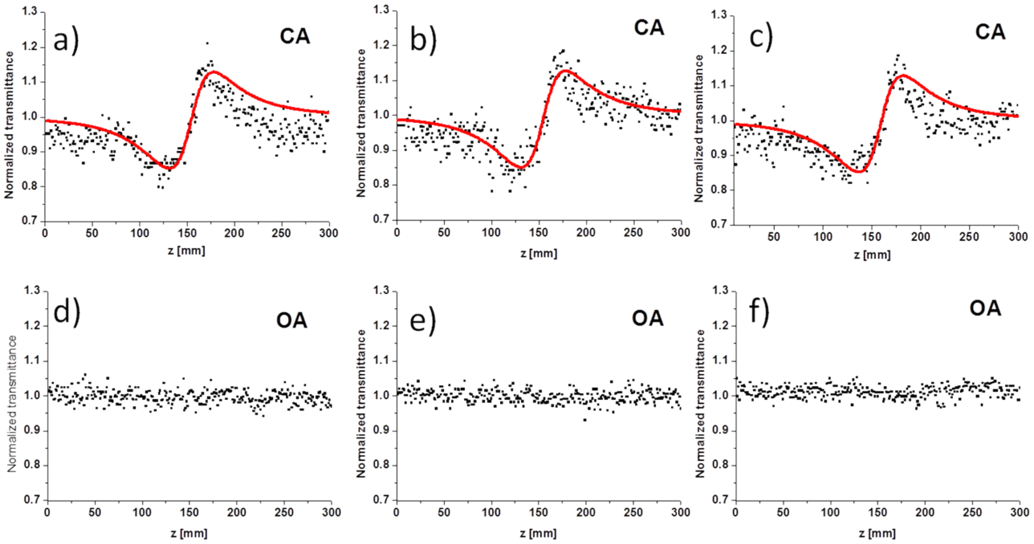

Fig.S 2 Representative Z-scan traces and theoretical fits for silica (a), solvent (b), uncoated silica nanospheres (120nm) (c), closed-aperture (CA) ; d), e), f) corresponding open-aperture traces (OA), at 530nm.