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Scattering enhancement in colloidal metal–organic composite aggregates

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ABSTRACT

In analogy to metal nanocomposites, the investigated hybrid organic–inorganic aggregates induce an enhancement of the scattered light. To explain the observed broadening of the absorption band and the wavelength dependence of the scattering, the systems can be considered as a nanoparticle composite. The scattering enhancement obeys the scaling law with the same optical spectral dimension $d_0 = 0.3$ as that obtained through numerical simulations on cluster–cluster aggregates of purely metal nanoparticle composites.

1. Introduction

In colloidal aggregates of metal nanoparticles composite the local electric field at some nanoparticles differs significantly from the bulk, giving rise to scattering enhancement [1–3]. This phenomenon is associated with optical excitation of surface plasmons that are collective electromagnetic modes. Moreover, in fractal nanocomposites which do not have translational invariance, the collective excitations tend to be localized in sub-wavelength regions, called *hot spot*, where the electromagnetic field can be enhanced by several orders of magnitude (originating a strong Rayleigh and Raman scattering). Although the hot zones are localized in nanometric regions, they overall fill the cluster size, due to the simultaneous excitation of a group of eigenmodes by the external field. Therefore, when the frequency of the illuminating field is close to the frequency of the dipolar eigenmodes of the system, the dipole–dipole interaction gives rise to a strong scattering enhancement [3,4]. These hot spots originate large fluctuations of the local electromagnetic fields and one of the known effect is the surface enhanced Raman scattering (SERS), especially useful in sensing applications. Metal nanoparticle, for instance, can increase the excitation rates of chromophores and can alter their radiative and nonradiative decay rates [5]. Chromophores near hotspots effectively absorb more light and both their quantum yield and lifetime are affected.

Optical properties of nanostructured and fractal aggregates have been intensively investigated from the theoretical point of view and also under resonance conditions. The hot zones, for instance, can be experimentally measurable by near-field techniques, whereas far-field techiques like optical microscopy and micro-Raman spectroscopy give information in which the hot zones and spectral features are averaged out.

Also nanoantennae, made of paired metal nanoparticles, can support localized surface plasmon resonance and produce *hot spot* [6,7], useful for SERS [8,9] and enhanced fluorescence [10–12]. Asymmetrical nanoparticle dimers, on the other hand, offer new opportunities for photonic applications and their properties of second harmonic generation depend more strongly on polarization and symmetry of the local fundamental field distribution than on the nanogap size [13]. Among metal nanoparticles, cluster arrays composed of noble metal nanoparticles sustain near-field coupling between nanoparticles on multiple length scales (intracluster and intercluster separation), generating a multi scale cascade field enhancement [15].

Recently aqueous solution of organic fractal aggregates [15–17] based on cationic porphyrin ($TPPS_4$) and spermine also showed optical enhancement of the electromagnetic field. In analogy to metal nanocomposites, the three-component hybrid organic–inorganic system [18] based on gold nanoparticles (Au-NP) with spermine and porphyrin induces an extra enhancement of the Rayleigh and Raman scattered light. This enhancement is

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