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Shift of localized surface plasmon resonance in monolayer of small gold nanoparticles: Simulation predictions of interparticle coupling

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ABSTRACT

Localized surface plasmon resonance of gold nanoparticle layer is investigated by the experiment as well as theoretical calculations. The limits of analytical models are illustrated for compact nanoparticle film revealing signify cant discrepancy between experimental and simulated results while the numerical calculations based on finite-difference time-domain using thin film optical parameters are shown as suitable. There it is shown that 3D finite-difference time-domain simulation can be replaced by 2D simulation without losing accuracy of the calculation of localized surface plasmon resonance. The dependence of the localized surface plasmon resonance wavelength on the nanoparticle size, separation as well as local dielectric constant of surrounding environment is presented and applied for the real nanoparticle size and separation distributions observed in the experiment. Tuning of plasmon resonance in a wide range is demonstrated as a promising way for further applications.

1. Introduction

During the last decades the surface plasmon effect observed on thin metal films attracted much attention in material research due to potential applications in electronics, photonics and sensors [1]. For each selected wavelength, the localized surface plasmon resonance appears for a specific incident angle only and it has been shown that it depends on properties of the surrounding environment [2]. However, recent progress in preparation of nanometer-scale structures revealed presence of surface plasmon polaritons, where plasmon resonance is no more dependent on the incident angle, but it appears for a certain wavelength λ only. In other words, these metallic sub-wavelength nanostructured materials exhibit induced dipoles (or higher orders) due to incident electromagnetic wave [3,4] at a specific resonance wavelength. The localized plasmon resonance in metal nanoparticles can cause near field enhancement and enhanced scattering cross section and both of them can be used to enhance performance of either detectors or emitters. This plays a key role for envisioned applications in organic electronics such as organic light-emitting diodes [5–7] or organic solar cells [8] as well as molecular biosensing [9–11]. Hence, the adjustment of the localized surface plasmon resonance started to be an important topic of the design and

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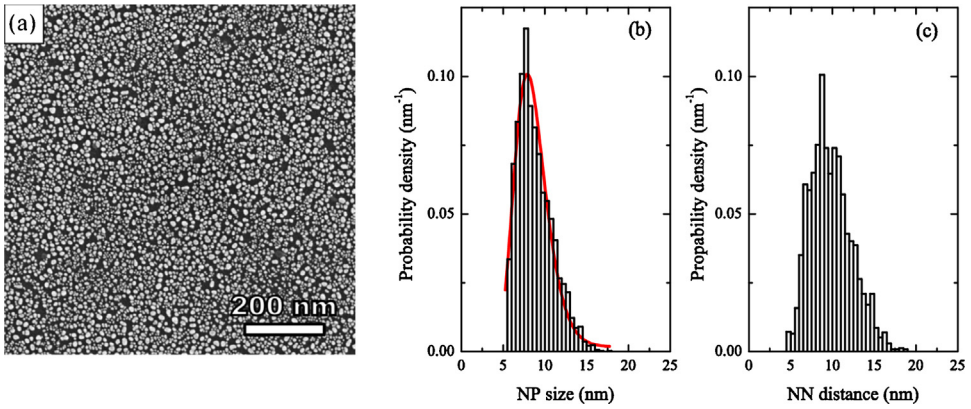

Fig. 1. (a) SEM image of the gold NP Langmuir film. Statistical analysis of SEM image of (b) NP size and (c) nearest neighbour (NN) distance. Solid line stands for fit of the log-normal NP size distribution.

technology [12]. It has been found in the experiments that the plasmon resonance of nanoparticles (NPs) depends on many parameters [13,14], such as NP shape and size [15], separation of NPs [12,16,17], or dielectric constant of the environment [18]. The explanation of the plasmon resonance of NPs has been obtained by the Mie analytical approach for single particle [19] and later extended to the generalized multiparticle Mie theory (GMM) [20]. Analytical calculations have been followed by more sophisticated numerical methods such as discrete dipole approximation (DDA) also called coupled-dipole method (CDM) [21] and recently also by the boundary element method (BEM) [22] and by the finite-difference time-domain (FDTD) numerical method also [23]. However, the relation between the ideal and real NP films is still an open question. In this work we discuss limits of the analytical approach such as Mie's quasi-static approximation of the electric field approach and demonstrate capability of numerical solution. It is shown here that bulk optical parameters are suitable for NP plasmonic effect calculations and there is no need to introduce effective size-dependent optical parameters. The dependences of the localized surface plasmon resonance wavelength on the NP size, separation and the dielectric constant of the environment are investigated. Furthermore, as an extension of these already known dependences the impact of the real NP size and separation distribution on plasmonic resonance is demonstrated and discussed.

2. Experimental

2.1. Materials and langmuir film preparation

Gold nanoparticles encapsulated in alkylthiols (PlasmaChem, Germany) were dissolved in chloroform (Sigma-Aldrich) prior the spreading on the water subphase (18.2 M cm, Elga, Bucks, UK) of the Langmuir trough using a microsyringe (Hamilton, Reno, NV). The total working area of the Langmuir trough (model 601 M, Nima Technology, Coventry, UK) was 86 cm^2, and the compression rate was set to 5 cm^2/min. The monolayer was allowed to equilibrate for 30 min before the compression. This time was found to be suficient for the solvent evaporation and monolayer formation. The surface pressure area isotherm was measured by the Wilhelmy plate method using a surface pressure sensor PS4 (Nima Technology). The modified Langmuir-Schaffer method (horizontal precipitation) was used for the NP monolayer deposition at the pressure of 10 mN/m. The NP size and spatial distribution were characterized by using the InLens detector of a field emission gun scanning electron microscope (SEM, LEO 1550) and analyzed by the Lispix software [24]. Fig. 1(a) demonstrates SEM image obtained on homogeneous close-packed NP film. The determined average NP size d is about 8 nm and the average interparticle distance L (*i.e.* centre-to-centre distance of nearest neighbor) is about 10 nm as it is demonstrated by statistical analysis, Fig. 1(b) and (c). The separation of NPs Δ, which is understood as a gap between two NPs ($\Delta = L - d$), reaches value of about 2 nm and agrees with published x-ray scattering measurements of Langmuir films [25].

2.2. Optical properties measurements and simulations

The optical properties were investigated by the AvaSpec-2048 Fiber Optic Spectrometer (Avantes company) in transmission setup. Extinction spectrum of gold NP film is depicted in Fig. 2(b). The FDTD modeling and simulations were performed by using the FullWAVE software package provided by the RSoft company [26]. The simulations were performed in the 2D projection as a one-dimensional chain of NPs as well as in 3D as a NP monolayer with hexagonal spatial order. The periodic boundary conditions ensure infinite length of NP chain (infinite area of NP monolayer in the case of the 3D modeling), while absorbing perfectly matched layer (PML) boundary is present in wave propagation direction. The spatial resolution was defined by the uniform grid with the step of 0.25 nm in all directions. Simulations of spectra were performed with the 60 meV energy step.