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Plasmon coupled nanoparticle arrays for fluorescence, photoluminescence and Raman scattering enhancement.

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Abstract. We study the enhancement of the fluorescence and photoluminescence by large homogeneous arrays of plasmon coupled 5-8 nm Au and Ag nanoparticles separated by distances less than 10 nm. A red shift of the major “symmetric” plasmon mode near 780 nm, and additional “anti-symmetric” plasmon mode centered near 310 nm evidence the plasmon coupling in Au particle arrays. The systems were found to be effective in enhancement of the fluorescence/photoluminescence processes.

1. Introduction

The ability of plasmon nanoparticles to concentrate electromagnetic radiation in the near field makes them a powerful probe to study ultralow concentrations of chemical and biological species by surface enhanced Raman scattering (SERS), fluorescence or chemiluminescence imaging [1-4]. Electromagnetic field redistribution in the vicinity of a single plasmon nanoparticle may cause a quenching or enhancement of molecule fluorescence [5]. The metal nanoparticle may change i) a local field distribution and ii) increase the intrinsic decay rate of the fluorophore. Thus, the total effect of the particle on the fluorescence is a superposition of two factors, notably, stronger excitation rate and the increase of the quantum yield (QY) / decrease the fluorescence lifetime [6-8]. When the electric field is M times enhanced near the isolated nanoparticle, which is not plasmon coupled with others, a Raman cross section of scattering molecule is enhanced by a factor of $\sim |M|^4$, whereas the fluorescence cross-section of the species is increased $\sim |M|^4/|M_d|^2$ times. Here $|M_d|$ denotes an amplification factor of the excited state decay rate for a molecule in the vicinity of a nanoparticle. More specifically, when for instance, a phosphor molecule is in the immediate vicinity of a 40 nm silver particle, i.e. the distance is $\sim 5\text{\AA}$, $|M|^2$ factor reaches a value of 20-40, whereas $|M_d|^2 \sim 10^6$. Thus, one can expect a fluorescence quenching by a factor of $\sim 10^3$ compared with the free-molecule case [9,10]. With increasing the particle-molecule distance to $\sim 8-10$ nm the fluorescence cross section is increased and passes through the maximum because $|M|^4$ decreases more rapidly than $|M_d|^2$ [6,9]. Still, M is not too high at any distance from a single spherical nanoparticle and, thus, large Raman enhancement does not occur and one can expect only a moderate fluorescence enhancement at a distance of $\sim 5-10$ nm from the metal particle [5]. The local electromagnetic fields are completely changed when the distance between adjacent particles becomes smaller than ~ 10 nm and the plasmon modes of single nanoparticles become coupled [11]. So-called “hot spots” in percolation films and “self-similar” nanoparticle arrays are discussed since the pioneer paper by Li et al. [12], further theoretically characterized in [13,14] and are summarized in review [15]. The considerable shift of the “symmetric” plasmon resonance band from 500 nm to 1500 nm and appearance of another band in the UV-green of an “anti-symmetric” plasmon mode in strongly coupled ~ 80 nm



particle assemblies with inter-particle spacing of $\sim 1\text{-}2$ nm was recently demonstrated by Hanske et.al [16]. Gaint SERS and fluorescence enhancement induced by strongly coupled nanoparticles using precisely controlled nano-engineering were demonstrated only a few years ago [8,17]. More specifically, a 473-fold fluorescence enhancement for fluorophore with $QY=0.3$ was reported for Au dimers with gap distance of ~ 6 nm [17] and more than 1000-fold fluorescence enhancement near nanorod for low QY (1.9-2.5%) [18]. Electron beam lithography is normally used to design plasmon nanoobjects in precisely controlled way but on small area. In particular, an array of bowtie nanoantennas with a gap down to 6 nm was presented recently [11]. Self-assembling techniques namely nanosphere lithography and template assisted assembling [16], drying of colloids [19], use of ligands to produce nanogaps [20] and other deposition techniques allow design quasi-homogeneous arrays of nanoparticles on the large areas. We study the capability of vacuum based methods such as pulsed laser deposition (PLD) and magnetron sputtering to design large homogeneous arrays of plasmon coupled Ag and Au nanoparticles for fluorescence enhancement and SERS.

2. Experimental

The special feature of nanoparticle arrays morphology produced by depositing a metal film in vacuum and Ar gas were characterized using FE-SEM Zeiss SUPRA 25. Optical absorption spectra were studied using UV/Vis Spectrophotometer Varian 5000. The influence of Au particle arrays on the fluorescence of Rhodamine B dye and on the ZnO photoluminescence were studied under excitation at 514 nm (Ar⁺ laser) and at 325 nm (He-Cd laser), correspondingly. The spectra were detected by using Renishaw inVia Reflex Raman spectrometer with spectral resolution better than 1 cm^{-1} . All the samples were excited at normal angle to the substrate with the fluorescence/PL emission being collected in the backward direction. As a metal-enhanced fluorescence has a radiation pattern with maxima in forward and backward directions one may expect that $\sim 50\%$ of emitted light was collected. The areas with/without nanoparticles were prepared on the same substrate and the identical measurement conditions were used to minimize an uncertainty.

3. Results and discussion

To illustrate the influence of the ambient gas on the nucleation of a metal film we studied in-situ the PLD growth of semi-continuous Au film in vacuum (10^{-5} mbar) and in Ar (0.7 mbar) atmosphere at room temperature. Laser ablation was done by focusing a KrF (248 nm, 10Hz) laser beam on a rotating target to give a fluence of $\sim 2\text{ J cm}^{-2}$ on a 10 mm^2 rectangular spot. For deposition in vacuum a target to substrate distance was 5 cm. The DC resistance of the Au film growing in vacuum on ZnO/a- Al_2O_3 substrate was measured in situ as a function of laser pulse number (Figure 1). With increasing deposited material and fractional coverage f , nanoparticles grow to reach a percolation threshold at $f=f_c$. As the film keeps growing the isolated nanoparticles ((1) in Figure 1) transform to a semi-continuous ($f>f_c$) ((2, 3) in Figure 1) and, finally, a continuous ($f=1$) film at an equivalent mass thickness more than 10 nm. The percolation threshold for Au films in the discussed deposition regime corresponds to $\sim 100\text{-}200$ laser pulses.

When ablating Au in the heavy ambient gas such as Ar, one may easier obtain more homogeneous arrays of $\sim 5\text{-}8$ nm Au nanoparticles separated by distances less than 10 nm. The number of laser shots corresponding to percolation threshold is $\sim 600\text{-}800$ pulses in this case. The vacuum chamber was evacuated down to 2×10^{-4} mbar and an Ar flow was introduced to maintain a pressure of 0.7 mbar. Au particles were deposited at room temperature. A reduced target to substrate distance of ~ 3.5 cm was used, which roughly corresponds to stopping distance of a laser plume at this pressure. An array of “small” Au nanoparticles less than 10 nm separated by gaps less than 10 nm is obtained for 500 laser shots (Figure 2a).

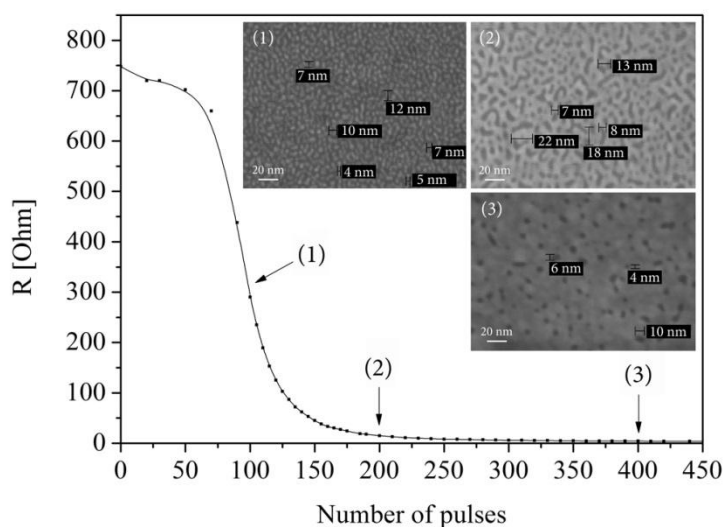


Figure 1. The DC resistance of the growing Au film on ZnO/a-Al₂O₃ substrate measured in situ as a function of laser pulse number. SEM images (1)-(3) of the samples deposited for respective number of laser shots are shown in the inset.

Ag nanoparticle arrays were deposited by DC-magnetron sputtering at room temperature (Figure 3a). A rotating substrate was maintained at 8 cm from the Ag (99.8%) target. Ag films were deposited at 3.2×10^{-2} mbar of Ar ambient pressure. The discharge voltage and current were maintained at to be 100 V and 35 mA, respectively.

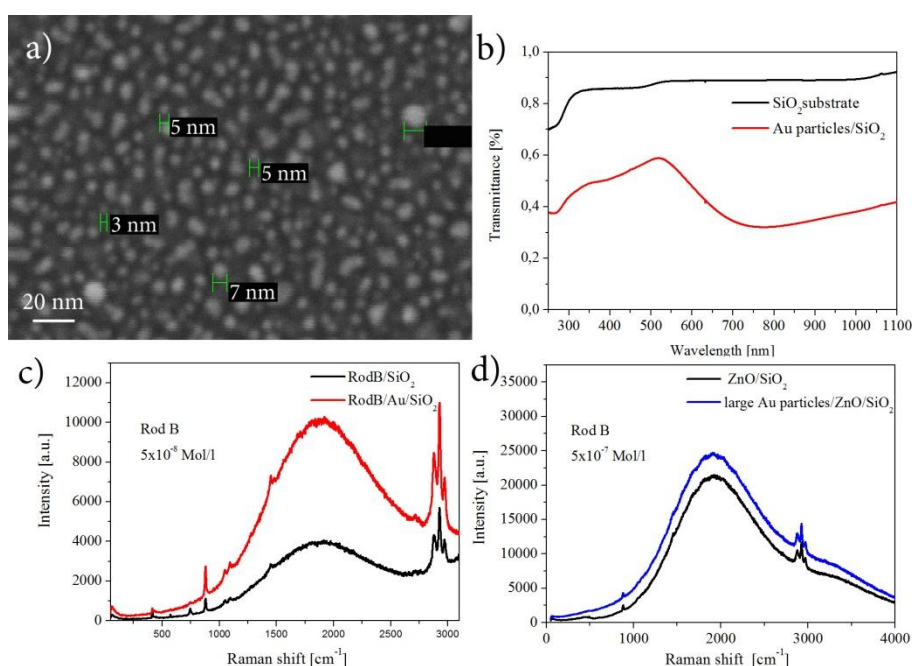


Figure 2. A typical Au nanoparticle array produced by PLD in Ar gas at 0.7 mbar (a); optical absorption spectra of “small” plasmon coupled nanoparticles (b); fluorescence of Rod B and Raman scattering enhanced by the array of “small” nanoparticles; minor effect of “large” not coupled nanoparticle array on fluorescence (d)

Optical absorption spectra of isolated small Au nanoparticles normally show a single major plasmon resonance peak near 520 nm. Higher energy shoulder is often attributed to $d \rightarrow sp$ transitions of gold. Still, additional plasmon mode caused by plasmon coupling may also appear in this range when the inter-particle distance is reduced to nanometers [13]. Absorption spectra of Au nanoparticle array onto SiO_2 substrates deposited in Ar gas revealed two plasmon bands evidencing that plasmon coupling occurs (Figure 2b). More specifically, a major “symmetric” plasmon mode is shifted to red and appears near 780 nm, whereas additional “anti-symmetric” plasmon mode was centered near 310 nm [13,14]. Similar increase of optical absorption in the UV range can be followed in spectra presented in several previous studies of strongly plasmon coupled nanoparticles, namely in [18,16], but the origin of such behavior was not discussed there.

Similar, Ag nanoparticle arrays deposited onto ZnO films show plasmon coupling behavior. Apart from the major plasmon resonance near 500-530 nm an additional broad band in UV/blue region with photon energy higher the band gap of ZnO was observed (Figure 3b, c). In the case of silver the d -band of the ground state is completely separated from the sp -band, thus the $d \rightarrow sp$ transitions show higher photon energies than those of Au. Thus, the observed increase of the optical absorption in the UV region is likely originated from the “beginning” of the plasmon coupling rather than from the $d \rightarrow sp$ transitions [14]. For Ag particle array a “symmetric” mode is shifted to lower photon energy for ~ 57 nm and ~ 35 nm with increase of Ag content in the case of particle arrays on SiO_2 and ZnO surfaces, respectively (Figure 3b, c). The UV broad band corresponding to “anti-symmetric” plasmon mode becomes more pronounced with increase of Ag content for both cases (Figure 3b, c).

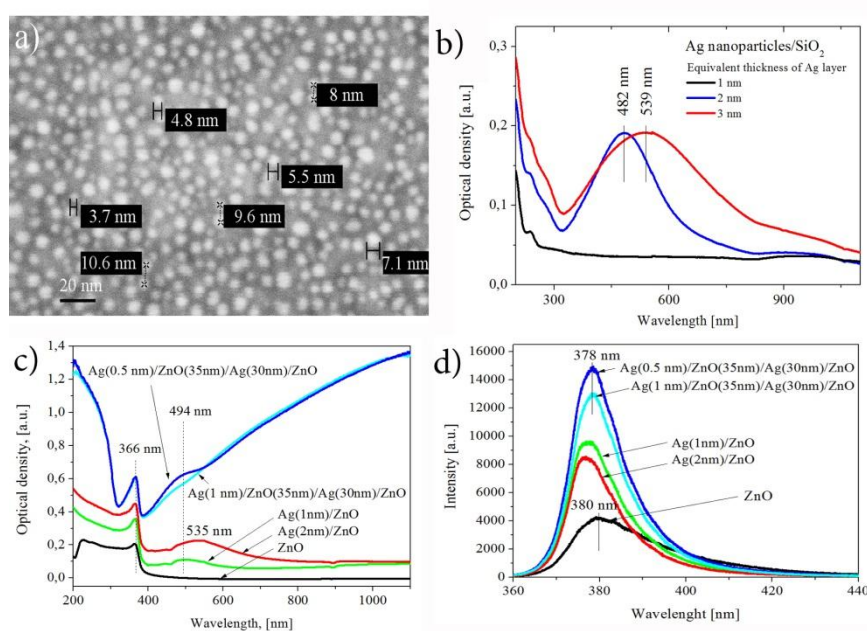


Figure 3. SEM image of Ag nanoparticle array (a), optical density of Ag particles on SiO_2 (b), optical density of Ag particles onto ZnO (substrate subtracted) (c), and ZnO photoluminescence enhanced by Ag particles (d).

We examined the effect of “small” nanoparticle arrays on the fluorescence of Rhodamine B (Rod B) dye dissolved in the ethanol with concentrations of 5×10^{-5} – 5×10^{-8} Mol/l. The fluorescence self-quenching is insignificant at such Rod B content [21]. Rod B molecules have an optical absorption in the range of 480-560 nm with a maximum near 550 nm and a fluorescence in the

range of 530-630 nm with maximum near 569 nm. Thus, we use Ar⁺ laser light (514 nm) to excite fluorescence of Rod B dye.

Both Ag and Au nanoparticle arrays were found to be capable to enhance fluorescence/ photoluminescence cross-section concentrating the electric field near the surface in the gaps between the particles. In particular, the detected fluorescence of a Rod B (5×10^{-8} Mol/l) was ~2.55 fold and Raman modes of dye and ethanol were more than ~2.3 fold enhanced by “small” Au nanoparticle array (Figure 2c), whereas a homogeneous array of “large” (~40 nm) well separated (not coupled) nanoparticles does not show or show minor (~1.4 fold) enhancement (Figure 2d). This supports our assumption that our “small” particle arrays are plasmon coupled systems, though the coupling is not too strong yet.

As noted above the plasmon coupled particles enhance fluorescence enhancement by i) concentrating the local electric field intensity in gaps, i.e. by increase of the excitation rate of a fluorophore ii) by increasing the quantum yield/decreasing the fluorescence lifetime. The first effect is optimal when the absorption of fluorophore is maximal at the wavelength of the plasmon resonance. On the other hand spectral overlap between plasmon mode and fluorophore emission spectrum should also have overlap. The most fluorescence enhancement is expected to the red of the plasmon resonance [22]. The efficiency of the two effects is defined by geometry of an array, position of fluorescent molecule, by the overlap between plasmon modes and absorption/emission spectra of fluorophore and by its initial quantum efficiency. We believe that the geometry on an array may be further optimized by adjustment the deposition conditions to diminish the inter-particle gaps. Note, that in present study optical absorption of a “small” Au nanoparticle array has a minimum near ~520 nm and the “symmetric”/“anti-symmetric” plasmon modes have lower/higher photon energy, which is not optimal to enhance a fluorescence of Rod B. Rod B has high quantum yield of ~65%, which is already high, and this value can't higher than 100%. Thus, we expect that the discussed nanoparticle arrays would be more effective to enhance the fluorescence of chemical and biological species with better overlap of particle plasmon bands and absorption/emission spectra of fluorophore. Fluorophores with low QY may also help better characterize the ability of the arrays and is the subject of further study.

To further enhance the efficiency to detect fluorescence and Raman response we designed a two sandwich-like structures of Ag particles/ ZnO(35nm)film/Ag(30nm)/ZnO(200nm)/a-Al₂O₃ by DC-magnetron sputtering and PLD methods. The Ag “mirror” was separated from the particle array to effectively collect a light emitted in backward direction. The 35 nm thick ZnO spacer was deposited at room temperature. The equivalent thickness of the top Ag layers was calculated to be 1 and 0.5 nm.

Ag nanoparticle arrays without “mirror” show ~2 fold enhancement of ZnO exciton photoluminescence (Figure 3d). Using a sandwich-like structure with Ag “mirror” under the Ag particle array the ZnO photoluminescence was further enhanced and the PL response was ~3.5 times higher in comparison with pure ZnO layer.

In summary we studied the possibilities to produce a plasmon coupled nanoparticle arrays by PLD and magnetron sputtering techniques. Absorption spectra of arrays of “small” Au nanoparticles less than 10 nm and separated by less than 10 nm gaps revealed two plasmon bands evidencing that plasmon coupling occurs. The fluorescence of a Rod B dye molecules (5×10^{-8} Mol/l) is ~2.55 fold enhanced by the “small” particle array. The 1.5 fold higher efficiency to collect the fluorescence response by use of Ag “mirror” under the particle array is demonstrated.

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