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Giant Rabi splitting in metal/semiconductor nanohybrids

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ABSTRACT

We present strong coupling regime between localized plasmon in lithographed nanoparticles and excitons in an organic semiconductor. The lithographed nanoparticles allow a very good control of the particle size and environment, thereby avoiding a large inhomogeneous broadening of the plasmonic resonances which could partially mask the plasmon/exciton hybridization. The nanoparticles diameter ranges from 100 to 200 nm. A giant Rabi splitting energy of 450 meV is obtained, and typical behaviors of mixed states, i.e. anticrossing of their energies and crossing of their linewidths, are observed. Three-dimensional finite-difference time-domain simulations and coupled oscillator calculations are used to analyze and corroborate the experimental results.

1. Introduction

Metallic nanoparticles support the localized surface plasmon which can be used to tailor the optical properties of an emitter located near the nanoparticle. For instance, luminescence [1,2] and Raman enhancement have been evidenced and applied to high efficiency light emitting diodes [3] and single particle Raman measurements [4,5], respectively. When the optically active material in the vicinity of the metal present high oscillator strength, a strong coupling regime between plasmons and excitons can be reached, leading to the formation of mixed plasmon/exciton states; an anticrossing in the dispersion relations is then observed, the strength of the coupling being characterized by the Rabi splitting. This hybridization has been predicted theoretically for metallic nanoparticles

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interacting with an emitter [6], where well-separated mixed states and a clear anticrossing have been observed. From an experimental point of view, the strong coupling regime has been demonstrated for delocalized plasmons on planar metal surfaces with a Rabi splitting energy of 300 meV [7,8], on nanostructured metal surfaces [9,10], and on close packed nanorods [11]. For localized surface plasmons (LSP) in metallic nanoparticles, luminescence enhancement has been observed in the weak coupling regime [12], as well as coherent effects [13]. The formation of mixed plasmon/exciton states with a Rabi splitting energy of 120 meV has been demonstrated recently in metallic nanoshells coupled to molecular exciton [14].

In this work, metallic nanodisks (NDs) organized in arrays by lithographic means covered by an organic semiconductor are studied. Lithographed structures is allow a fine control of the size of the nanoparticles and of their environment (other particles and semiconductor), thereby avoiding a large inhomogeneous broadening of the plasmonic resonances, which could partially mask the plasmon/exciton hybridization. The obtained Rabi splitting energy is extremely large (450 meV). This unique property arises from the combination of very large excitonic oscillator strength and a considerable enhancement of the electromagnetic field due to the LSPs. The strength of the plasmon/exciton coupling observed here indicates that the formation of mixed states probably occurs in various types of hybrid metal/semiconductor nanosystems, influencing their emission properties. Systems where the Rabi splitting represents a significant part of the transition energy [15] are also of interest for the creation of correlated photon pairs sources [16].

2. Sample fabrication and characterization

The Ag NDs were deposited on a microscope slide, thoroughly washed prior to the processing steps (in acetone and acid baths). The Ag NDs' patterns have been defined by e-beam lithography. A 60 nm thick silver film was evaporated and then removed by the lift-off technique, hence revealing the silver ND assemblies on the surface. Each assembly consists of a 200 by 200 μm array made of several tens of thousands of NDs separated by 200 nm, side to side (Fig. 1(a)). Several arrays, with different nanoparticle diameters, were fabricated, on the same microscope slide, in order to tune the LSP resonance energy. The nanoparticle sizes range from 100 to 210 nm, corresponding to an aspect ratio varying from 1.7 to 3.5. Scanning electron microscope (SEM) images of the nanoparticles were taken to determine the mean particle diameter and the ND size dispersion. A SEM image is shown in Fig. 1 as well as a typical size dispersion of NDs with a 140 nm mean diameter. The typical size dispersion is $\pm$7 nm and the distance between the NDs is 200$\pm$7 nm side to side. This distance has been chosen to cause a negligible interaction between the localized plasmons of neighboring NDs, in order to drastically limit the influence of the environment on the coupling between the plasmon of a single disk and semiconductor excitons. Indeed, the interdisk coupling becomes negligible when the disk diameter is lower than the separation distance [17]. The influence of the array on the coupling effect described in the following is therefore negligible. Diffractive effects can also be observed in periodic nanoparticle array [18], which can result in the apparition of sharp peaks in the optical spectra [19]. However, to observe such peaks the nanoparticles have to be imbedded in a homogeneous medium, as shown by Auguie et al. [19], which is not the case in our experiments where the nanodisks are surrounded by glass on one side and air or dye on the other sides.

All the transmission experiments reported in this work were done at room temperature on circular regions of 50 μm diameter (probing around 2×10^4 identical NDs) under an incident light propagating perpendicular to the sample plane. Fig. 2(a) shows the transmission spectra recorded for three arrays having three different ND diameters. A pronounced dip is observed for each array, its spectral position changing with the ND diameter. This dip is associated to the ND localized surface plasmon resonance. No dependence on the incident light polarization was observed, a good indication of the particle circular isotropy. The plasmon resonance energy, measured from the transmission minimum, is plotted in Fig. 2(b) as a function of the disk diameter. It shifts from 1.8 to 2.45 eV while its width remains quasi-constant, about 180 meV. This linewidth includes both a homogeneous and an inhomogeneous broadening. The latter mainly arises from the gaussian ND size distribution and can be deduced from the dispersion measured from the SEM images ($\pm$7 nm) and the size/energy relation extracted from Fig. 2(b). This inhomogeneous broadening is estimated to 90 meV. Supposing that the