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Surface Plasmon Assisted Directional Rayleigh Scattering

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The origin of the Rayleigh scattering ring effect has been experimentally examined on a quantum dot/metal film system, in which CdTe quantum dots embedded in PVP are spin-coated on a thin Au film. On the basis of the angle-dependent, optical measurements under different excitation schemes (i.e., wavelength and polarization), we demonstrate that surface plasmon assisted directional radiation is responsible for such an effect. Moreover, an interesting phase-shift behavior is addressed.

Key words: Surface plasmon, Directional Rayleigh scattering, Quantum dot, Metal film

I. INTRODUCTION

As is well known, surface plasmon (SP) describes a class of transverse magnetic polarized optical surface waves that propagate along a metal-dielectric interface and whose fields are coupled to the metal’s charge density oscillations [1–5]. By virtue of the unique properties of SP, such as strong electromagnetic field enhancement, subwavelength localization, and high sensitivity to the bounding dielectric environment [5], the past decade has witnessed great advances in many newly emerging, SP-related (or usually called plasmonic) fields, including nanophotonics [6], metamaterials [7], biosensing [8], and imaging [9], etc. Among a variety of fascinating, plasmonic effects discovered to date, an interesting phenomenon termed as SP-coupled emission (SPE) has received much attention [10–20]. For most SPE-related studies, the investigated systems were fluorescent organic dye molecules coupled to the SP of a thin metal film [10–18], in which the highly p-polarized, directional fluorescence emission was found to be identical to that of the fluorophore. The p-polarization and angular dependence of SPE turned out to be consistent with radiating plasmon, i.e., the reverse process of SP absorption. Apart from these fluorophore-based SPE studies, the multiplexing capability and sensitivity of SPE were found to be dramatically improved by using quantum dots (QDs) instead of fluorophores as probes [19, 20]. For both systems, the physics behind the occurrence of highly directional and strongly enhanced SPE can be understood as a result of near-field interactions between the excited species (fluorophores or QDs) and the SP at the metal thin film. Noticeably, when performing a set of QD-based SPE measurements to understand how the SP of metal surface influences the optical emission of QDs and how the QD/metal heterostructure affects the reflectivity of the excitation beam, Gryczynski et al. observed another ring-shaped radiation pattern whose wavelength is identical to that of the excitation laser, Gryczynski et al. observed another ring-shaped radiation pattern whose wavelength is identical to that of the excitation laser, in addition to the directional SPE of interest [19]. They claimed that the exact mechanism underlying such sort of Rayleigh scattering ring effect was unclear; nevertheless, they suspected that the QDs might assist in the coupling of scattered light (Rayleigh-type) to SP [19].

To look into the origin of this Rayleigh scattering ring effect, we here report our experimental investigations on a typical QD/metal system, in which CdTe QDs embedded in PVP are spin-coated on a thin Au film. From a set of angle-dependent, optical measurements under different excitation schemes (i.e., wavelength and polarization), we demonstrate that SP-assisted directional Rayleigh radiation accounts for this effect.

II. EXPERIMENTS

The CdTe QDs were synthesized through a documented procedure [21]. In a typical synthesis, NaHTe solution was first prepared. To obtain NaHTe solution, 335 mg of Te powder was treated with 400 mg of NaBH4 pre-dissolved in 5 mL water under N2 atmosphere for 3 h. Cd source solution was prepared by dissolving CdCl2(1/2)H2O (273.5 mg), 3-mercapto-1-propanol (200 μL), and NaOH (220 mg) in H2O (36.5 mL).
NaHTe solution (0.5 mL) was injected into Cd source solution, and the mixture was raised to 90 °C and kept for 6 h under N$_2$ protection with stirring. Finally, the mixture of CdTe and polyvinylpyrrolidone (PVP) aqueous solution was spin-coated on an Au film (Zolix) and then heated to form a drying film.

The scanning electron microscope (SEM) images of Au film and CdTe QDs (PVP) film are shown in Fig.1 (a) and (b), respectively. The roughness of the 50-nm-thick Au film was ~2 nm. Although the CdTe QDs (PVP) films were found to be agglomerated, their formation appeared uniform and the QDs were well distributed under large-field optical observation. The high-resolution transmission electron microscopy (HRTEM) images of CdTe QDs are shown in Fig.1 (c) and (d). The size of CdTe QDs was ~4 nm, from which one can clearly see the (111) lattice planes of CdTe with a lattice spacing of ~0.37 nm (in agreement with that of CdTe bulk crystal, refer to JCPDF No.75-2083).

The excitation light sources used in our optical measurements included a He-Ne laser (25-LHP-151-230, CVI) and a tunable optical parametric amplifier (TOPAS-C, Coherent) pumped by a femtosecond Ti:Sapphire regenerative amplifier (SH-1207K5-2-25, Harmonic laser, center wavelength ~800 nm, pulse duration ~50 fs, pulse energy ~3 mJ). The polarization of the laser beam was adjusted by jointly using a Glan-Taylor prism and a half-wave plate. The scattered light was delivered to a spectrometer (USB4000, Ocean Optics).

III. RESULTS AND DISCUSSION

The optical layout used in this work is schematically illustrated in Fig.2(a), in which two excitation schemes (using a p-polarized He-Ne laser) are depicted, with I and II denoting reverse Kretschmann [15] and Kretschmann [19] configurations, respectively. As shown in Fig.2(b), under both I and II schemes an obvious ring-shaped pattern was observed. Note that under scheme II the ring position kept fixed when the incident angle of the excitation beam was varied in a certain range that is larger than the total reflection angle of the hemispherical glass substrate. The intensity of the scattered light from the ring turned out to peak at a collecting angle of ~47°, as displayed in Fig.3(a). This angle was found to nicely match the minimum reflectivity angle observed in another parallel experiment that measured the dependence of the excitation-light reflectivity on its incident angle (see Fig.3(b)). Remarkably, the two, mutually consistent angles (~47°) are also in agreement with the angle that characterizes the SP excitation according to the well-known equation

$$\theta_{SP} = \sin^{-1}\left[\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}\right]$$

where $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of the medium and the sample, respectively, and $n_1$ is the index of refraction of the medium.
FIG. 3 (a) The intensity of the scattered light from the ring vs. the collecting angle $\theta$. (b) The dependence of the excitation-light reflectivity on its incident angle.

FIG. 4 The intensity of the scattered light from the ring vs. the collecting angle $\theta$, obtained under three different excitation wavelengths (633, 680, and 800 nm). Inset: comparison between experiment and simulation.

where $\varepsilon_1$ and $\varepsilon_2$ denote the dielectric constants of glass and Au, respectively, and $n_1$ is the refractive index of glass. These results suggest that the observed directional Rayleigh scattering ring effect most likely correlates with a sort of SP-assisted radiation.

In addition to the above single-wavelength (633 nm, He-Ne laser) experiment, we have also conducted similar measurements using a tunable femtosecond laser as an excitation source. The results obtained under three different excitation wavelengths (633, 680, and 800 nm) are exhibited in Fig.4, the inset of which gives a comparison between experiment and simulation. The consistency suggests again that the observed directional, ring-shaped Rayleigh radiation can be ascribed to an intrinsic, SP-related effect.

Considering that the SP occurring on the metal-dielectric interface is essentially an evanescent electromagnetic wave whose $k$-vector (electric field) is parallel (perpendicular) to the interface (Fig.5(a)) [1–4], we took a further step to examine the polarization dependence in the directional Rayleigh scattering ring observations. The optical layout we used is shown in Fig.5(b), which allowed for polarization-dependent coincidence measurements.

FIG. 5 (a) Schematic illustration of the SP occurring on a metal-dielectric interface. (b) The optical layout for the polarization-dependent coincidence measurements.

FIG. 6 (a) The polarization dependence of SPCE with respect to the following two cases: collecting the scattered light from the Rayleigh scattering ring vs. collecting the grazing light under $p$- or $s$-polarization excitations. The corresponding observation data are plotted in Fig.6, in which the fitting results are also given. Notably, the $I$–$\alpha$ relationship for the cases shown in Fig.6 (a) and (b) is in phase, while that for the cases shown in Fig.6 (a) and (c) is out of phase by $45^\circ$ (corresponding to a $90^\circ$ phase shift in terms of polarization, simply because $\cos^2\alpha=(\cos 2\alpha+1)/2$). It is known that the $p$-polarization and angular dependence of SPCE are indicative of the radiating plasmon [19]. Similarly, the above observations of in-phase (for $p$-polarization) and out-of-phase (for $s$-polarization) behaviors further support that the Rayleigh scattering ring effect should arise.
as a result of the SP-assisted radiation when the p-polarization excitation feature of SP and the significant local-field enhancement of SP (Fig. 6 (a) and (b)) is taken into account. Interestingly, the observed 90° phase shift in polarization echoes well to the anisotropic intensity pattern of the Rayleigh scattering ring (i.e., alternating bright and dark distributions by 90°).

IV. CONCLUSION

Through a set of wavelength- and polarization-dependent, optical measurements on a model system of CdTe quantum dots/Au metal film, we have experimentally evidenced that the origin of the Rayleigh scattering ring effect is surface plasmon assisted directional radiation. This work provides complementary insights into the well addressed subject of surface plasmon coupled emission.

V. ACKNOWLEDGMENTS

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