Enhanced luminescence by second-harmonic surface plasmon resonance

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Abstract—Strong ultraviolet luminescence having intensity comparable with device-quality GaN epilayers has been observed in Au nanoparticles. It is identified that the luminescence involves radiative recombination of electrons in band 6 (sp conduction band) with holes in band 4 (secondary top d band), near the L symmetry point. We show that the strong emission is a consequence of the second-harmonic surface plasmon resonance (SHSPR), which is an inherent nature of metallic nanoparticles with high density of surface plasmons. For the SHSPR, we only need a weak pumping source to trigger the second harmonic absorption of very dense surface plasmons in Au nanoclusters. In addition to emissions of Au nanoparticles, SHSPR provides a very efficient way to enhance the luminescence of composites with metal nanoparticles. Incorporation of Au nanoparticles into SiO₂ nanoparticles can enhance the luminescence intensity by two orders of magnitude. SHSPR can serve as one of the underlying mechanisms responsible for surface-enhanced nonlinear optical phenomena.

I. INTRODUCTION

The discovery of surface-enhanced spectroscopy has stimulated enormous excitement [1,2]. Through its various progeny, it has served as an impulse that has resurrected activity in electromagnetism, changed the momentum in nonlinear optics, electrochemistry [3], and surface science, etc. Various models have been proposed to interpret the enhancement [1,4-8]. Some involve the chemical effect which is referred to molecular interaction between molecules and metal surface [1]. Others suggested the electromagnetic effect which depends on the electromagnetic interaction between molecules and metal surface [4-8]. However, it is difficult to understand how the optical transition can have its intensity enhanced by 10^6 through molecule-metal interaction but keep its transition energy fixed [4]. We report a mechanism arising from second harmonic surface plasmon resonance (SHSPR) which can serve as a possible route responsible for the large enhancement. In addition to the observation of strong UV luminescence arising from Au nanoparticles, we demonstrate that SHSPR can be used to enhance the luminescence intensity of SiO₂ nanoparticles by two orders of magnitude.

II. EXPERIMENTAL RESULTS

Metal nanoparticles [9-11] obtained by different synthesis methods were used to obtain the photoluminescence (PL) and photoluminescence excitation (PLE) spectra. 18 nm Au nanoparticles reveal a significant absorption peak at 526 nm, which indicates the surface plasmon resonance through the nanoparticles.

Fig. 1 shows the PL spectra of 18 nm Au nanoparticles excited by various radiations with different wavelengths. The peak intensity at 350 nm can be greatly enhanced when the wavelength of excitation is at around 250 nm. The sharp peak on the short wavelength shoulder is due to the Raman scattering of intermolecular stretching of OH band [12]. The other signals arise from Au nanoparticles since they are absent without Au nanoparticles. Theoretical PL calculation was given by Boyd et al.[13]. After the absorption, the excited electrons and holes will relax from their initial excited states to new energy states via the scattering, and the luminescence results from the radiative recombination of these relaxed carriers. The peak at 350 nm can be attributed to the transition of electrons from 6 sp conduction band to holes in the top 4 d band, near the L symmetry point. The peak at 425 nm refers to the radiative recombination of electrons in 6 sp conduction band with holes in the top 3 d band near the X symmetry point [13].

Fig. 1. Emission spectra of Au (18 nm) nanoparticles with increasing incident wavelength from $\lambda = 250$ nm to 300 nm.

The integrated PL intensity of Au nanoparticles is comparable with that of the device quality GaN epilayers which are capable of a strong UV emission at room temperature. The PL measurements for Au films were performed with different surface conditions. PL intensity can be greatly enhanced for rough Au films. This implies that surface roughness may play an important role in the enhanced luminescence.

For the PLE spectrum, it is clear that there exists a sharp peak at around 255 nm, which is about one half of the wavelength of surface plasma. This provides an important clue that the enhanced PL intensity excited by 250 nm radiation as shown in Fig. 1 is a result of second harmonic surface plasmon resonance (SHSPR).

Fig. 2. The photoluminescence (PL) spectra of SiO₂ nanoparticles with and without Au nanoparticles.

Interestingly, we have performed the same experiment for 13 nm Au nanoparticles. It indicates that the PLE peak does blue shift according to the second harmonic frequency of surface plasmon. From the above results, we may conclude that the strong UV emission of Au nanoparticles at room temperature is a consequence of SHSPR. Here, Au nanoparticles provide the very dense surface plasmons which are required for the generation of second harmonic absorption. The absorbed electromagnetic wave is localized near the metal surface, and thus enhances the efficiency of the subsequent emission.

The so called generation of second harmonic has been applied to demonstrate the strong enhancement in thin films and nanoparticles [14,15]. With coupling of surface plasmons via surface roughness, second-harmonic generation (SHG) can be enhanced by several orders. The internal generation of second harmonic photon was ruled out since SHG is not allowed in bulk gold due to the centrosymmetry. It has been demonstrated that two-photon excited interband photoluminescence (PL) can also be strongly enhanced at rough thin films or at nonsymmetry interfaces [16]. For SHSPR to occur, we only need a very weak pumping source. The very dense quantum particles required to generate second harmonic absorption preexist in the studied materials such as surface plasmons in Au nanoparticles. The weak external radiation with frequency equal to the second-harmonic frequency of a particular resonance of the dense quantum particles is used to stimulate the second harmonic transition. Large enhancements can be produced when the material absorbs the photon and localizes it. The fact that metal particles absorb the photon and store the electromagnetic energy into surface plasmons can serve as an excellent example. This increases the electromagnetic energy density near the surface, and hence the enhancement occurs. Indeed, following the usual simple derivation in nonlinear optics, the nonlinear polarization P of second-harmonic absorption can be written as [14,17].

$$\vec{P}(2\omega) \approx \alpha_{eff} (\vec{\nabla} \cdot \vec{E}) \vec{E} + \beta_{eff} (\vec{E} \cdot \vec{\nabla}) \vec{E}, \quad (1)$$

with α_{eff} and β_{eff} are coefficients characteristics of the metal. At the second harmonic resonance, α_{eff} and β_{eff} become resonantly enhanced, and hence the corresponding electromagnetic field.

The effect of SHSPR was used to perform the PL experiment for SiO₂ nanoparticles [9-11] with and without the incorporation of Au nanoparticles (7 nm) as shown in Fig. 2. With the insert of Au nanoparticles into SiO₂ nanoparticles, the PL intensity of SiO₂ nanoparticles can be enhanced by a factor more than 100 due to the effect of SHSPR. We thus demonstrate that SHSPR provides one of the excellent alternatives to elucidate surface-enhanced spectroscopy.

III. SUMMARY

We have demonstrated unambiguously that second harmonic surface plasmon resonance in metal nanoparticles can localize electromagnetic field near surface and lead to a large enhancement of light absorption and emission. In addition to the strong UV emission observed in Au nanoparticles, the luminescence of SiO₂ nanoparticles incorporated with Au nanoparticles can be enhanced by a factor of 100 due to SHSPR. We point out that SHSPR can serve as one of the underlying mechanisms to elucidate surface-enhanced nonlinear optical phenomena.

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