PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **3** No 2, 02MAN04(4pp) (2014)

Surface Plasmon Enhanced Photoluminescence of Rhodamine 6G on Au Nanoparticles 2D Array: Temperature Effects

O.A. Yeshchenko, I.S. Bondarchuk, V.V. Kozachenko, M.Yu. Losytskyy

Physics Department, Taras Shevchenko National University of Kyiv, 64/13 Volodymyrs'ka Str., 01601 Kyiv, Ukraine

(Received 20 June 2014; published online 29 August 2014)

Influence of temperature on the photoluminescence of rhodamine 6G deposited on 2D array of the gold nanoparticles was studied in the temperature range 78–278 K. The factor of surface plasmonic enhancement of rhodamine luminescence was found to decrease monotonically with increasing temperature. Electron-phonon scattering and thermal expansion of the gold nanoparticles were considered as two competing physical mechanisms of the temperature dependence of plasmonic enhancement factor. The calculations showed the significant prevalence of the electron-phonon scattering that causes the temperature induced decrease of plasmonic enhancement of rhodamine 6G luminescence observed.

Keywords: Gold nanoparticles, Surface plasmon resonance, Rhodamine 6G photoluminescence enhancement, Temperature effects.

PACS numbers: 73.20.Mf, 78.67.Bf, 78.55.–m

1. INTRODUCTION

Noble metal nanoparticles (NPs) exhibit unique optical properties, such as resonant absorption and scattering of light, not found in bulk counterparts [1]. Collective coherent excitations of the free electrons in the conduction band are responsible for the strong absorption and scattering of the light by the particles. These coherent oscillations, also known as Surface Plasmon Resonance (SPR), lead to an enhanced local electric field close to the surface of the particles [1]. Such strong local electric field enhances the optical processes such as Raman scattering (SERS), absorption (SEIRA) and photoluminescence (SEPL), etc. of molecules and clusters functionalized on the surface of metal nanoparticles or close to a rough metal surface.

The influence of the NP's size on plasmonic enhancement of SERS and PL from the molecules adsorbed on the rough metal surfaces and on the surface of metal NPs as well as on PL from the metal NPs themselves was studied quite well. Meanwhile, the influence of temperature on the phenomena of plasmonic enhancement is still open for study. In general, understanding the influence of temperature on the SPR in metal NPs and related phenomena, including the effect of SPR induced enhancement of the various optical processes mentioned above, is crucial for pure and applied science involving NPs.

Recently, we reported the temperature dependence of the quantum yield of the PL from silver [2] and copper [3] NPs. In present work we studied the influence of the temperature on the plasmonic enhancement of PL from the object external to the metal NP. As such an external model object we have chosen the rhodamine 6G (R6G), a well-known dye widely used in many areas of fundamental and applied science.

2. SAMPLE PREPARATION AND CHARACTERIZATION

The samples were prepared as follows. Four glasses plates with area 1x1 cm^2 were cut from the same plate. Gold film with thickness of 5 nm was fabricated by thermal vacuum deposition on two glass plates at the same time. Then this Au film was annealed at a temperature of 370 °C during half an hour. The annealing leads to transformation of the gold film to array of the gold NPs. The existence of Au NPs on glass substrate was confirmed by atomic-force microscopy (AFM) (Fig. 1). The samples studied were found to contain the Au NPs with average height about 10 nm, while average lateral size was about 25 nm. Then, one of obtained sample with gold NPs array and one of remaining initial glass substrate were covered by rhodamine 6G/ shellac hybrid film with a thickness of 10 nm at the same time. We used hybrid film because molecular aggregates of R6G, in the form of dimers or higher aggregates, act to quench photoluminescence. This quenching process is mainly due to the transfer of excitation energy between monomers and aggregates, which then decay non-radiatively. Thus, we had four samples. The first is initial glass plate, the second one – gold NPs on glass, the third – R6G/shellac film covering gold NPs, and the fourth – R6G/shellac film on glass.

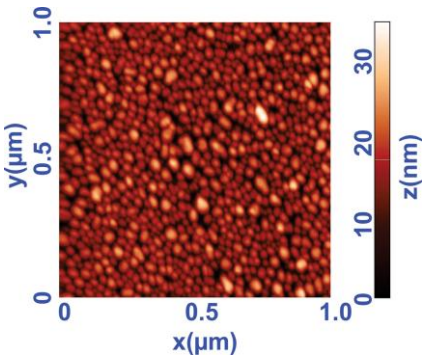

Fig. 1 – AFM image of Au NPs array on glass substrate.

3. RESULTS AND DISCUSSION

The main role of this work was to study the temperature effects in the influence of the SP field on the

PL spectrum of R6G deposited on Au NPs array. Figs. 2 and 3 show the behaviour of the PL spectrum of hybrid R6G/shellac film and one deposited on the gold NPs array correspondingly with the monotonous increase of temperature from 78 to 298 K. Note, all the spectra presented in Figs. 2 and 3 belong to R6G species. Indeed, the spectra of Fig. 3 were obtained by subtraction of the PL spectrum of shellac film on glass from the total PL spectrum and the ones of Fig. 4 – by subtraction of the spectrum of shellac film on Au NPs array. It is seen that PL spectra of R6G both without the gold NPs and deposited on Au NPs array consist of three bands denoted as M_l, D_l, and C_l. Following the data of Refs. [4,5], the M_l one with maximum at 570 nm originates from the light emission from the single R6G molecules, the D_l one (605 nm) is due to PL from R6G dimers, and C_l (635 nm) is the PL band of R6G aggregates. Note that in PL spectrum of R6G species in shellac on glass the M_l band of single rhodamine molecule is quite intensive, its intensity is comparable with ones of dimers and aggregates. Meanwhile, the deposition of the R6G/shellac film on the Au NPs array leads to appreciable decrease of the molecule M_l band intensity with synchronous increase of the intensity of D_l and C_l bands related to R6G aggregates. Probably, the higher intensity of PL from rhodamine aggregates in sample with Au NPs can be explained as following. The increase of the temperature leads to red shift of SPR, i.e. to the shift towards the D_l and C_l bands. Such shift would lead to higher overlap of the SPR in Au NPs and the PL bands of rhodamine aggregates causing the higher plasmonic enhancement of intensity of the respective D_l and C_l bands.

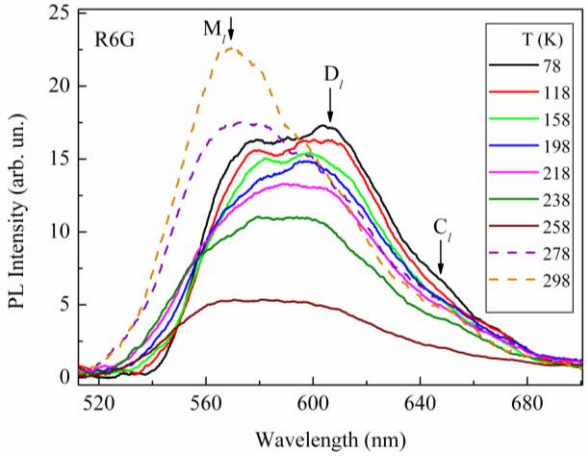

Fig. 2 – Evolution of PL spectrum of R6G/shellac thin film with monotonous increase of temperature from 78 to 298 K.

One can see from Fig. 2 that the dependence for R6G without gold NPs is slightly decreasing in temperature range 78–198 K and becomes sharply decreasing in the range 198–258 K that is in full agreement with data reported in Ref. [6]. Meanwhile, the further increase of the temperature from 258 to 298 K leads to abrupt change of the intensity decrease to its sharp increase. It is seen (Fig. 3) that qualitatively similar dependence is observed for R6G on gold NPs array. Note that increase of R6G PL intensity at increase of the temperature in the range 258–298 K is accompanied by sharp increase of intensity of molecular (monomer) M_l band and simultaneous sharp decrease of dimer and aggregates D_l and C_l ones, Figs. 2 and 3. Based on this, one can suppose that such PL intensity increase with temperature is caused by thermally induced dissociation of R6G aggregates that leads to increase of the number of free rhodamine molecules. It is well known that the PL quantum yield decreases at the aggregation of rhodamine molecules. Thus, thermally induced increase of number of R6G free molecules would lead to increase of the quantum yield of all the rhodamine species and, correspondingly, to the increase of their PL intensity.

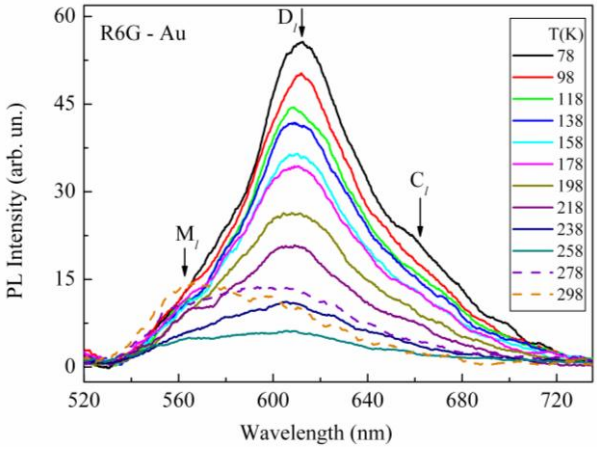

Fig. 3 – Evolution of PL spectrum of R6G/shellac thin film deposited on Au NPs array with monotonous increase of temperature from 78 to 298 K.

It is quite interesting the temperature dependence of the ratio of PL intensity of R6G on Au to one of R6G without Au, Fig. 4 – blue points and line. One can see that this ratio decreases monotonically with temperature. Let us analyse the cause of such interesting effect. The R6G molecules in sample with Au NPs array are located in the local field of surface plasmons excited in gold nanoparticles. The plasmonic electric field enhances the PL from rhodamine. Thus, one can conclude that difference in the temperature dependence of PL intensity from R6G on Au NPs and one from R6G without them is caused by the temperature dependence of the plasmonic enhancement factor of PL from R6G. The magnitude of enhancement factor is determined by the magnitude of plasmonic field in vicinity of R6G molecules located near Au NPs. So, let us consider the physical mechanisms that can cause the temperature dependence of the magnitude of the plasmonic field.

It is well known that optical transitions in molecules and clusters located near the surface of metal NPs are strongly enhanced. Such enhancement is caused by a strong local electric field near the metal NP where surface plasmons are excited. Thus, tuning the magnitude of plasmonic enhancement gives the opportunity to tune the magnitude of the optical response of such molecules and clusters. According to Boyd's theory [7], the local electric field outside a metal NP is enhanced by a factor known as the local field correction factor

$$L_{out} = \frac{\varepsilon}{\varepsilon_m} \frac{D^{-1}}{\frac{\varepsilon}{\varepsilon_m} - 1 + D^{-1}\left[1 + i\frac{4\pi^2 V(1-\varepsilon)\varepsilon_m^{1/2}}{3\lambda^3}\right]} \qquad (3.1)$$

where D is the depolarization factor ($D = 1/3$ for spherical particles), ε is the dielectric permittivity of the metal particle, ε_m is the dielectric permittivity of the surrounding medium, λ is the light wavelength, $V = \pi d^3/6$ is the NP volume, and d is its size (diameter). The intensity of PL $I(\omega_l)$ from a molecule located near the metal NP excited with a photon of energy $\hbar\omega_{exc}$ is given by

$$I(\omega_l) = I_0(\omega_l)\left|L^2(\omega_{exc})L^2(\omega_l)\right|, \qquad (3.2)$$

where $I_0(\omega_l)$ is a function describing the intrinsic PL spectrum of the molecule, i.e. in the absence of metal NP. The plasmonic factor L depends on T due to temperature dependence of dielectric permittivity of NP ε and NP's volume V.

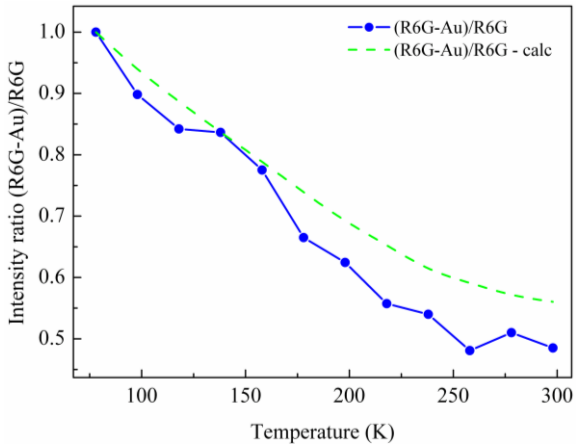

Fig. 4 – Temperature dependence of the ratio of PL intensity of R6G on Au to one of R6G without Au: experimental – blue points and solid line, and calculated – dashed green line.

Based on theoretical model considered in details in Ref. [2] we calculated the PL spectra of R6G on Au NPs influenced by SP field at various temperatures in range of 78–298 K. The obtained behaviour of the spectra is shown in Fig. 5. One can see that calculated temperature evolution of PL spectrum of R6G on Au NPs array is in good agreement with experimental one (Fig. 3) that proves correctness of the used theoretical model. The good agreement is obtained as well for the experimental and calculated temperature dependences of the ratio of PL intensity of R6G on Au to one of R6G without Au, Fig. 4. One can see that the dependence of the ratio is monotonically decreasing with temperature. This indicates the fact of monotonic decrease of plasmonic enhancement factor with temperature. Let us discuss it.

As one has been discussed above, the temperature affects both the SPR width and frequency. The temperature dependences of both width and frequency are caused by two physical mechanisms. Those are the electron-phonon scattering and the thermal expansion of metal NP. The SPR width is caused the plasma oscillation damping constant. The increase of temperature leads to increase of electron-phonon scattering rate and, correspondingly, to increase of SPR damping. Meanwhile, the temperature increase leads to the thermal expansion of the NP which leads to decrease of the rate of electron surface scattering and, correspondingly, to decrease of damping constant. However, as we have shown in our previous works [8] the contribution of the electron-phonon scattering in the temperature dependence of SP damping constant exceeds greatly the one of the surface scattering.

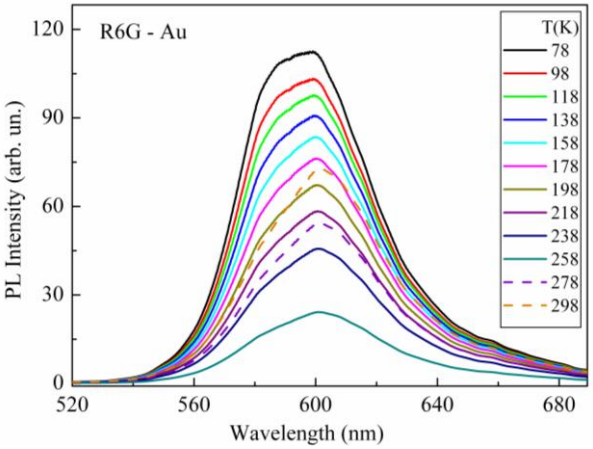

Fig. 5 – Calculated evolution of PL spectrum of rhodamine 6G on Au NPs array with monotonous increase of temperature from 78 to 298 K.

As well, the thermal expansion of NP leads to red shift of SPR. The red shift of SPR with increasing temperature occurring due to NP expansion would increase the overlap of SPR (maximum at 543 nm at 298 K) and PL bands of R6G with maxima at 570 nm, 605 nm and 635 nm. This effect would lead to increase of plasmonic enhancement factor and, correspondingly, would lead to the increase of R6G PL quantum yield. Note, however, that the spectral separation of the SPR in Au NPs and PL spectrum of R6G is quite large. So, it is reasonably to expect that this effect is not so much to affect significantly the plasmonic enhancement factor. Besides this, an additional mechanism of the influence of temperature induced red shift of SPR on plasmonic enhancement factor exists. Hubentahl showed recently [9] that interband transitions are significant additional mechanism of SPR damping when SPR frequency is close to the onset of interband transitions. At photon energies higher than onset of interband transitions the energy of the plasmon can be transferred to a single electron, which makes an interband transition. It is clear that for photon energies well below the onset of the interband transition, the plasmon energy is too low to permit an interband transition and, correspondingly, such a mechanism of plasmon damping is not important. For bulk gold the onset of interband transitions is at about 660 nm. At wavelength shorter than 660 nm the increase of imaginary part of dielectric permittivity of gold ε_2 occurs that reflects the increase of contribution of the interband transitions. Note, however, that strong increase of ε_2 starts at $\lambda \leq$ 520 nm

while in wavelength range from 660 to 520 nm ε_2 increases quite slightly. It is obvious that the red shift of SPR with increasing temperature would lead to decrease of the contribution of interband transitions to plasmon damping constant at the frequency of SPR. Such a decrease of SPR damping would lead to the increase of plasmon enhancement factor and, correspondingly, to the increase of PL intensity. However, taking into account that SPR wavelength (about 540 nm) is in the range of slight spectral dependence of ε_2 (520 – 660 nm) it is reasonably to expect that this effect is not so much to affect significantly the plasmonic enhancement factor. Therefore, proceeding from above considerations one can conclude that the electron-phonon scattering is prevailing mechanism of the temperature dependence of plasmonic enhancement factor. Correspondingly, the temperature induced increase of electron-phonon scattering rate leads to decrease of quantum yield of PL from rhodamine 6G on gold NPs array. Note that this effect observed for Au NPs is opposite to one observed for the PL from copper NPs where the increase of temperature leads to increase of PL quantum yield [3]. An origin of such surprising behaviour of PL from copper NPs is that for Cu NPs the interband transitions and spectral overlap of SPR with PL band give considerably larger contribution in the temperature dependence of plasmonic enhancement factor than for gold NPs.

4. CONCLUSIONS

In conclusion, we made the comparative study of the temperature dependence of the PL from rhodamine 6G deposited on 2D array of gold NPs and PL from R6G without Au NPs in the temperature range of 78 – 298 K. The PL from R6G on Au NPs array is enhanced by the coupling of exciting and emitted photons to the surface plasmons excited in the NPs. There is a significant difference in the temperature behaviour of the PL spectra from R6G–Au and R6G samples. The ratio of PL intensity of R6G on Au to one of R6G without Au was found to be monotonically decreasing with temperature. This indicates the fact of monotonic decrease of the factor of plasmonic enhancement of PL from R6G on Au NPs with temperature. The theoretical model was proposed to explain the observed temperature dependence of plasmonic enhancement factor. Two possible physical mechanisms of the observed temperature dependence were considered. First one is the electron-phonon scattering which causes the increase of plasmonic damping constant with increase of the temperature leading to the weakening of the plasmonic enhancement. Second one is the thermal expansion of the gold NPs. The thermal expansion increases the NP size leading to decrease of the plasmonic damping caused by surface scattering of electrons and to corresponding strengthening of plasmonic enhancement. As well, the thermal expansion of Au NPs leads to red shift of SPR in Au NPs with increasing temperature. The red shift would cause the increase of the spectral overlap of SPR with PL band of R6G as well as decrease of the contribution of interband transitions in gold NPs in plasmonic damping constant. Thus, the temperature induced red shift of SPR would lead to the strengthening of plasmonic enhancement of R6G PL. The calculations of the influence of temperature on the PL spectrum of R6G in plasmonic field of Au NPs were performed. The results of calculations agree with the results of the experimental observations proving the model used. The calculations showed that the electron-phonon scattering is prevailing mechanism in the temperature dependence of the factor of plasmonic enhancement of PL from R6G on Au NPs as compared to effects related to the thermal expansion of Au NPs. Correspondingly, such prevalence of the electron-phonon scattering causes the temperature induced decrease of plasmonic enhancement of R6G PL observed.

AKNOWLEDGEMENTS

O.A. Yeshchenko and I.S. Bondarchuk acknowledge the partial support by the State Agency on Science, Innovations and Informatization of Ukraine (grant # M/325-2013).

REFERENCES

1. V.V. Klimov, *Nanoplasmonics* (Pan Stanford Publishing: 2013).
2. O.A. Yeshchenko, I. S. Bondarchuk, M.Yu. Losytskyy, A.A. Alexeenko, *Plasmonics* **9**, 93 (2014).
3. O.A. Yeshchenko, I.S. Bondarchuk, M.Yu. Losytskyy, (submitted to *J. Appl. Phys*.)
4. V.V. Bryukhanov, S.A. Elistratova, V.C. Laurinas, *J. Appl. Spectroscopy* **70**, 450 (2003).
5. G.S.S. Saini, S. Kaur, S.K. Tripathi, C.G. Mahajan, H.H. Thanga, A.L. Verma, *Spectrochim. Acta A* **61**, 653 (2005).
6. H.T. Oh, H.-S. Kam, T.Y. Kwon, B.K. Moon, and S.I. Yun, *Mater. Lett.* **13**, 139 (1992).
7. G.T. Boyd, Z.H. Yu, Y.R. Shen, *Phys. Rev.* B **33**, 7923 (1986).
8. O.A. Yeshchenko, I.S. Bondarchuk, V.S. Gurin, I.M. Dmitruk, A.V. Kotko, *Surf. Sci.* **608**, 275 (2013).
9. F. Hubenthal, *Plasmonics* **8**, 1341 (2013).