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Surface enhanced anti-Stokes one-photon luminescence from single gold nanorods

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Anti-Stokes one-photon luminescence from a single gold nanorod is experimentally investigated. The anti-Stokes emission of gold nanorods is enhanced and strongly modulated by localized surface plasmon resonance (LSPR). It is found that the polarization dependence of the anti-Stokes emission is in strong correlation with that of the Stokes emission. Further experiments provide evidence that LSPR significantly enhanced both excitation and emission processes. Moreover, the line shape of the anti-Stokes emission is dependent on the surface temperature, which is related to the distribution of free electrons near the Fermi level. This discovery provides an effective method in principle to probe localized temperature at nanoscale dimension. Here, the reported results about the anti-Stokes emission provide more understanding for the photoemission process from the plasmonic nanostructures.

Introduction

First, photoluminescence (PL) from smooth metal films was reported with quite low quantum yield (QY).[1] Later, PL from metallic nanostructures has been observed with considerably higher QY in comparison with the bulk material.[2–4] The light emission process is strongly related to the localized surface plasmon resonance (LSPR) of metallic nanostructures.[2–7] Recently, PL phenomena has received increasing interest for its potential applications in many fields, such as a bright photostable label, biological molecules recognition and orientation sensing, plasmonic modes characterization, and optical recording.[8–14] Moreover, the anti-Stokes light emission from metallic nanostructures, of which the emitted photons have a higher energy compared to the absorbed photons, were usually investigated with pulsed light sources such as two-photon luminescence.[8–10,15–19] Unlike the two-photon luminescence, the anti-Stokes one-photon luminescence receives considerably less attention and has only been studied in few studies. Using a cw laser excitation, previous reports have observed the anti-Stokes one-photon luminescence from an ensemble of gold nanoparticles and nanorods in solution,[20,21] and from rough gold thin films.[22] Nevertheless, systematic investigation and understanding of such anti-Stokes one-photon luminescence from a single individual plasmonic nanoparticle are lacking.

To date, previous studies on one-photon luminescence from single plasmonic nanostructures mostly concentrated on the Stokes emission.[11–13,23–26] In this study, we demonstrated that the Stokes emission from a single gold nanorod was always accompanied with a plasmonic surface enhanced anti-Stokes emission. In contrast to previous ensemble of measurements,[20,21] the anti-Stokes one-photon luminescence at single nanoparticle level provides us more knowledge about its origin. It was determined that both the anti-Stokes emission and the Stokes emission were polarization dependent and were significantly modulated by the LSPR of gold nanorods, indicating that both the processes are coherent. Moreover, the line shape of the anti-Stokes emission was strongly modulated by the thermalized electrons distribution near the Fermi level. This finding provides a method to optically probe nanoscale localized temperature of a nanoparticle. Furthermore, experiments tuning the resonance frequency of the same particle either through photo-thermal reshaping or changing environmental index have evidenced that LSPR considerably enhances both excitation and emission processes and remarkably increases the anti-Stokes emission intensity.

Experiments and discussion

A single particle microspectroscopy system based on a scanning probe microscope (NTEGRA Spectra, NT-MDT, Russia) was developed to combine the white light dark-field scattering, photoluminescence spectroscopy, and atomic force microscopy

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(AFM) techniques. The optical setup allows us to perform an *in situ* measurement to obtain the scattering and PL spectra of the same single nanoparticle. The setup has been described in detail in our previous reports.[11–13] In brief, the scattering spectra of nanoparticles were measured using a white light total internal reflection scattering method based on a high numerical aperture oil-immersion objective lens (NA 1.49, 60 × TIRF, Olympus, Japan). A collimated white light beam was approximately focused at the objective's back focal plane, and the scattering signal was collected by the same objective lens and directed into a spectrometer with a cooled CCD (iDdus, Andor). Moreover, the microspectroscopy system can easily switch to PL spectrum measurement excited by a cw laser at $\lambda = 632.8$ nm *in situ* for the same nanoparticle.

The gold nanorods investigated here were chemically synthesized,[27,28] and the inset in Fig. 1 shows a representative TEM image of the synthesized nanorods. The nanorods have short axes of 20–30 nm and longitudinal axes of 50–80 nm. The nanorods were immobilized onto a glass coverslip with an average interparticle spacing of several micrometers for single particle spectroscopy measurements.

To obtain one-photon luminescence, a cw He–Ne laser at wavelength 632.8 nm (photon energy ~1.96 eV) was used to excite the nanorods. Furthermore, Notch filters (NF03-633E, Semrock) were utilized to simultaneously obtain the Stokes and anti-Stokes emission. The scattering spectra were recorded *in situ* with dark field white light total internal reflection technique. All the spectra were measured at room temperature. The spectral shape of Stokes PL roughly resembles the scattering ones. The results agree well with previous reports for plasmonic nanostructures with simple geometrical shapes.[11–13,23,24]

Interestingly, a bright anti-Stokes emission always accompanied the conventional Stokes emission when the nanorods were excited by the 632.8 nm laser. A representative spectrum (containing both Stokes and anti-Stokes components) of one-photon luminescence from a single gold nanorod is shown Fig. 1. After comparing the spectra of many single individual nanorods, it was determined that the anti-Stokes emission intensity was significantly enhanced if the nanorod longitudinal LSPR matched rather than detuned away from the excitation laser frequency. To confirm the anti-Stokes signal, bulk silicon wafer and bulk gold (a magnetron sputtering target with smooth surface) were tested at the same experimental condition except for longer exposure time. The corresponding data are shown in the inset of Fig. 1. The background of the silicon spectra is low as expected. The three peaks can be attributed to 1st Stokes and anti-Stokes, and 2nd Stokes Raman scattering, respectively. The bulk gold presents not only the Stokes signal as in previous reports but also an obvious broadband anti-Stokes emission. These observations show that the anti-Stokes emission of the gold material are truly from the intrinsic optical property of the gold material itself. By roughly counting the excitation focus volume and original spectral intensity, the anti-Stokes emission brightness per gold atom of the nanorod is over 3 orders of magnitude higher compared to bulk material.

The anti-Stokes one-photon luminescence of gold nanostructures has been reported in previous studies, but the properties were not investigated and discussed in detail.[20–22] For instance, anti-Stokes emission from an ensemble of 25 nm diameter gold nanoparticles in solution was observed in ref. 20. The authors claimed that the spectral shape of one-photon luminescence was similar to the absorption spectrum.[20] Very recently, the study on an ensemble of gold nanorods in solution showed that the anti-Stokes spectrum can be well fitted by a thermal population of excitations.[21] In addition, an obvious anti-Stokes emission was detected from a rough gold film illuminated by a cw 780 nm laser.[22] Here, the anti-Stokes one-photon luminescence was studied at a single individual gold nanorod level. The dependence on the excitation power and polarization, and the collection polarization were systematically investigated.

The dependences of the PL intensity on the excitation laser power and polarization are shown in Fig. 2. Both the Stokes and anti-Stokes emission have approximately linear laser-

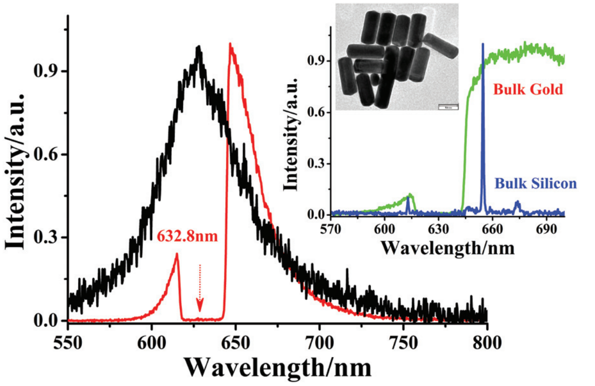

Fig. 1 Normalized scattering (black line) and PL spectra (red) of a representative gold nanorod. The inset presents the typical TEM image of the synthesized nanorods, and the emission spectra of bulk gold (green) and silicon wafer (blue) for comparison.

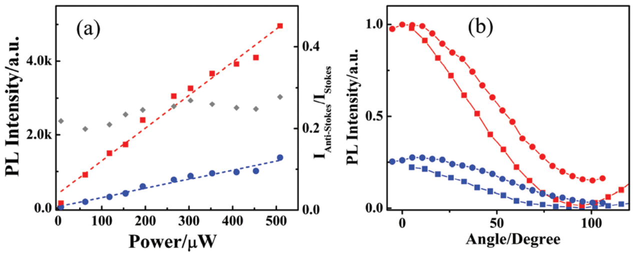

Fig. 2 Dependence of the PL intensity of a single nanorod on excitation laser power (a) and polarization (b). In (a), the Stokes (red squares) and anti-Stokes (blue circles) emission intensities linearly increase as the excitation power increases; moreover, the ratio of Stokes emission intensity to anti-Stokes one almost remains constant. The dashed lines are fitted curves. In (b), the Stokes (red) and anti-Stokes (blue) emission intensity present a correlated polarization dependence on the excitation polarization (squares) and collection polarization (circles).

power dependence. This indicates a *linear* one-photon excitation process [see Fig. 2(a)]. Instead, the ratio of the integrated Stokes emission intensity to the anti-Stokes one remains constant as the excitation power was increased. Using a $\lambda/2$ wave plate to tune the angle between excitation light polarization and the longitudinal axis of the nanorod, as seen from Fig. 2(b), the polarization dependence was observed. For the first time, we observed that the anti-Stokes emission is in strong correlation with the Stokes emission in polarization and followscos$^2\theta$ dependence, which is similar to the Stokes emission.[12,23] Both the anti-Stokes and Stokes emission intensity varied as the excitation polarization was rotated, and reached a maximum when the polarization of the excitation was parallel along the nanorod longitudinal axis. Moreover, the collection polarization dependence of the Stokes and anti-Stokes emission was also investigated. Next, the anti-Stokes emission behaves similarly as the Stokes emission, and the polarization of PL from the nanorod was always parallel to the longitudinal axes as an electric dipole radiation. This strong correlation indicates that both anti-Stokes and Stokes emissions share a common process and this process cannot be simply attributed to a pure thermal emission as previously stated.[15] All the results indicate that both Stokes and anti-Stokes emission are due to the same physical origin, *i.e.*, it should be strongly related to the LSPR of gold nanorods.

The spectral profile of the anti-Stokes emission is another interesting topic. As shown in Fig. 3, the intensity of anti-Stokes emission decays exponentially, to a good approximation, as photon energy was increased, which is consistent with a recent report of an ensemble of gold nanorods in solution, *i.e.* the line shape can be described by a thermal population of excitations.[21] This exponential decay behavior probably can be attributed to the distribution of thermalized electrons near the Fermi level. Generally, the sp-band free electrons can directly respond to optical radiation and rapidly decay due to the electron–electron and electron–phonon thermalization processes, which have been investigated using femtosecond pump-probe techniques.[29–32] In the present study, the electrons and lattice should reach quasi thermal equilibrium under the cw laser illumination, due to large electron population, high rate of electron–electron, and electron phonon processes.[2,30,31] The electrons occupation in sp-band near the Fermi level follows the Fermi–Dirac distribution, *i.e.* $\propto(1 + e^{-\Delta E/K_BT})^{-1}$. Here, the distribution can be simplified to follow Boltzmann statistic distribution $\propto e^{-\Delta E/K_BT}$approximately at room temperature.[21,25,29–32] Therefore, the line-shape of anti-Stokes emission is dominated by the thermal equilibrium electron distribution; moreover, the emission rate is also significantly enhanced by the LSPR of the nanorod. As seen in Fig. 3, the anti-Stokes emission as a function of the photon energy can be fitted well with Boltzmann statistics, but not Lorentzian, which is often effective for the Stokes emission.

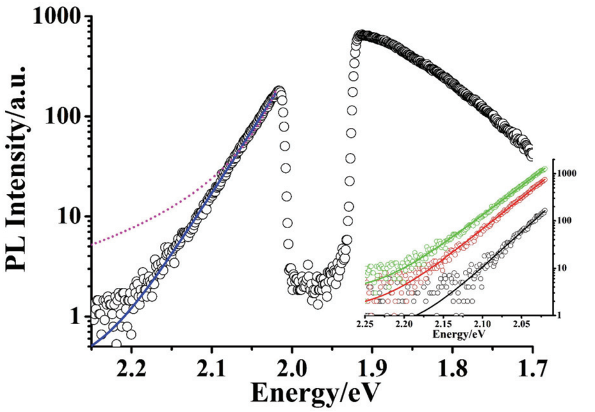

Fig. 3 Anti-Stokes emission as a function of photon energy. The data is fitted (lines) by Boltzmann statistics distribution (blue solid line) and Lorentz line shape (purple dashed line) for the anti-Stokes part, respectively. The inset presents anti-Stokes spectra at different illumination light intensities and corresponding fitting lines with Boltzmann statistics.

Furthermore, measuring the anti-Stokes spectrum provides us a method to probe the localized temperature at nanoscale. This nanoscale temperature optical sensing promises potential applications in many fields such as nanoscale biological temperature sensing. In the present case, the surface temperature of the nanorod under different illumination power can be extracted through fitting the anti-Stokes emission, as shown in Fig. 3 and ref. 32. For instance, ΔT (above room temperature) of about 65 ± 5 K, 126 ± 3 K, and 160 ± 2 K for excitation can be determined at 100 μW, 300 μW, and 500 μW, respectively. The nanorod photothermal reshaping was determined at $\Delta T \approx$ 180 °C, which is consistent with previous results.[24] Note that, the threshold temperature of photothermal reshaping for each individual nanoparticle varies from sample to sample because of the dispersion in size and shape. Therefore, the anti-Stokes emission from a single gold nanorod can provide an effective method in principle to sense a nanoscale localized temperature by fitting the anti-Stokes spectrum. Furthermore, efforts to demonstrate the ability of nanoscale thermometer are under way by adjusting the environmental temperature.

Furthermore, the experimental observation of anti-Stokes emission provides a good method to understand the PL process because of the low background on the anti-Stokes side. To date, it is widely accepted that LSPRs play an important role in the photoemission process of metallic nanostructures, although there is not an undisputed model for the process.[7,24,33,34] Two probable mechanisms, *i.e.* (i) plasmon-enhanced interband transitions of d-band electrons into sp-band and subsequent radiative recombination and (ii) the excited d-band holes recombine nonradiatively with sp-band electrons, and then emit plasmon particles, which subsequently radiate, have been proposed to explain the light emission.[7,21,22,24,33,34] The abovementioned two models based on e–h pair recombination scheme consider the excitation and emission process modified by the surface plasmon, respectively.

According to the experimental measurement of anti-Stokes emission, it is evidenced that the LSPRs of plasmonic nanostructures not only influence the excitation rate but also modify the emission efficiency. In this study, the sp-band free

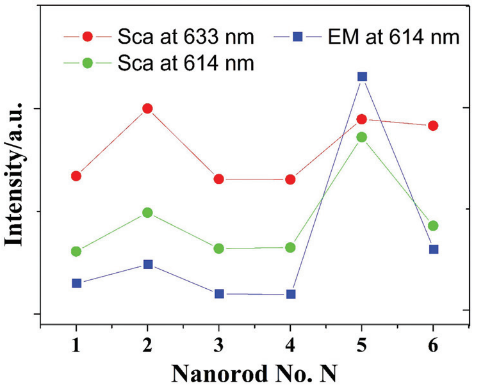

Fig. 4 Anti-Stokes emission intensities at a wavelength of 614 nm (blue), and the relative scattering intensity at a wavelength of 633 nm (red) and 614 nm (green) for 6 different individual nanorods excited by 633 nm laser, respectively.

electrons dominate the light emission process. The photon energy at wavelength 632.8 nm (or 780 nm in previous reports) is assumed to be unable to efficiently excite the d-band electrons (although the interband transition at X-point could be involved).[23] While the laser can couple with the sp-band free electrons directly and efficiently. Moreover, the sp-band free electrons are also strongly related to LSPRs due to electron collective oscillations. As can be seen in Fig. 1, the one-photon luminescence of the nanorods strongly correlates with the scattering spectrum. Thus, the excitation and emission processes are strongly modulated by LSPRs. More convincing evidences are demonstrated by correlating the original data of the scattering spectra and the PL spectra from different single nanorods. As shown in Fig. 4, the anti-Stokes PL intensity at wavelength of 614 nm from different shapes of nanorods follows the trend of the scattering intensities at excitation (at 633 nm), emission (at 614 nm), and their products. Clearly, the anti-Stokes emission is correlated with the scattering. In the present study, single nanorods being investigated had a narrow distribution of size and aspect ratio. The scattering and absorption cross-section can be approximately considered to linearly vary in the same trend in a narrow range.[35] Thus, the scattering intensity at 633 nm is approximately related to the absorption cross section of the nanorods. For emission process, the scattering intensity at 614 nm can be assumed to be proportional to the radiative rate of plasmon emission.[36] As a result, the relative anti-Stokes emission intensity of different individual nanorods can be roughly estimated, and then can be compared with the scattering intensities at the excitation and emission wavelengths. The experimental observations clearly indicated that LSPRs can enhance both the photon absorption and emission process during photoemission.

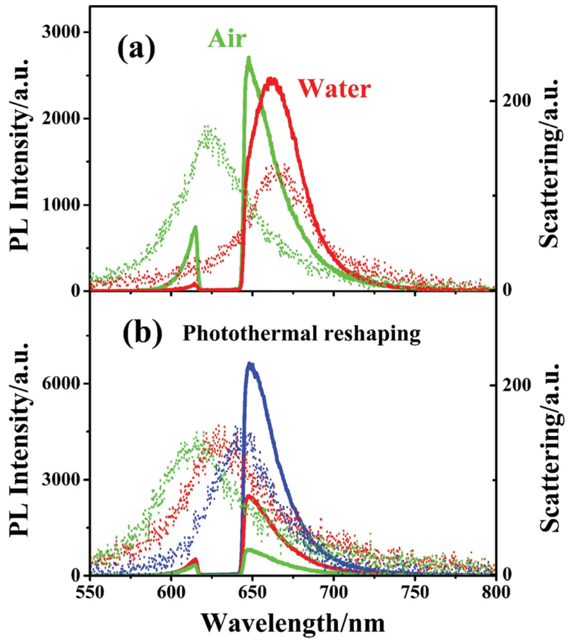

Fig. 5 Light emission spectra with change in local surface plasmon resonance frequencies. (a) The scattering (dots) and PL (solids lines) spectra of the same nanorod in air (green) and water (red). (b) The scattering (dots) and PL (solids) spectra of a single individual nanoparticle reshaped through photothermal effect. All the spectra were recorded after photothermal reshaping with the same excitation intensity.

To demonstrate the influence of LSPRs of the nanorod on the light emission, we adjusted the LSPR peak position of the same isolated nanoparticle, and measured the PL and scattering spectra *in situ*. The LSPRs peak of the nanorods were changed towards longer wavelength by increasing their environmental medium index, or can be tuned towards shorter wavelength by photothermal reshaping effects.[11,12,24] At first, the scattering and PL spectra of single nanorod were collected in air, and then measured *in situ* after immersing it in water as shown in Fig. 5a. It can be clearly seen that the anti-Stokes emission dramatically decreases as the LSPRs are red-shifted. The ratio of the anti-Stokes emission intensity to Stokes also considerably decreases due to less absorption and lower emission enhancement caused by LSPR. In addition, the laser heating effect was applied to induce a shape transformation of a nanorod towards a spherical shape. This reshaping results in the blue-shift of LSPRs. As seen in Fig. 5b, the scattering peak of the nanoparticle gradually blue-shifts but the intensity remains similar during the transformation of the nanorod to a sphere-like shape. This confirms that the volume of the particles is maintained. Thus, the absorption cross-section remains almost the same at the resonant frequency, but changes at excitation wavelength because the LSPR peak shifted away from the excitation wavelength. In contrast, the intensity of PL quickly decreases with photothermal reshaping due to the shape dependence of the quantum efficiency of the light emission. Our measurements were in good agreement with previous report that the QY decreases when the nanorod becomes a spherical nanoparticle.[24] Although the absolute intensity of anti-Stokes emission slightly decreases after photothermal reshaping, the ratio of anti-Stokes to Stokes emission intensity significantly increases after shape transformation because the Stokes emission dramatically decreases. In the end, the anti-Stokes emission efficiency becomes comparable to that of the Stokes emission because the LSPR peak overlaps well with the anti-Stokes emission band. All the results obviously verify that LSPR influences both the excitation and emission processes during the photoemission from the plasmonic nanostructures.

To date, there is not an undisputed model for the photoemission process of metallic nanostructures, although it is widely accepted that LSPR plays an important role in the process.[2,7,15,22,26,33,34] Generally, in metallic nanostructures, such as gold nanorods, the sp-band free electrons can directly interact with photons. In other word, it can be driven by a laser to collectively oscillate. Such collective oscillation of free electrons (COFE) in a metallic nanoparticle can radiatively emit photons as plasmon emission.[23,34] In order to understand both the Stokes and anti-Stokes emission, we propose a theoretical model by treating a single gold nanorod as a plasmonic resonator, supporting a quantized COFE. On the basis of the concept of the optical cavity, we model the PL of the single gold nanorod as the radiative emission of COFE from the nanorod's LSPR mode. Our model involves four processes: (i) the laser drives the COFE; (ii) the created COFE excites the LSPR mode as the input; (iii) the LSPR mode generates an output out of the COFE surrounding the surface of the nanorod; and (iv) the mode-generated COFE couples to the light and generates the photon emission. The detail description of the theoretical model is well-documented elsewhere.[32]

Specifically, the coupling efficiency between the light and the COFE is proportional with the spatial and temporal overlap of the modes. In addition, when a cw laser beam illuminates the gold nanorod, the sp-band free electrons gain energy, and then rapidly reach thermal equilibrium due to the fast electron–electron and electron–phonon interaction.[30,31] Then, the collective oscillation of free electrons involved in LSPR mode is modulated by the free-electron state density. In the thermal equilibrium, the electron state density often follows the Fermi–Dirac statistical distribution.[2,30] Therefore, the light emission process is related to both the sp-band free-electron distribution and localized surface plasmon resonance. Approximately, the distribution profile of the sp-band electrons under the Fermi level, which also modulates the Stokes emission, as a function of the photon energy, is flat. Therefore, the spectral line shape, which is dominated by the LSPR mode, adopts the Lorentzian profile. In contrast, for the anti-Stokes emission, the occupation profile of the sp-band electrons near or above the Fermi level is approximately a Boltzmann distribution, (the emission rate is enhanced in the same manner by the surface plasmon). Thus, the line shape of the anti-Stokes emission is governed by Boltzmann distribution. Our theory qualitatively explains the difference between the spectral line shapes of Stokes and anti-Stokes one-photon luminescence from single gold nanorods.[32] It also provides an understanding for the relation between the anti-Stokes spectral line shape and the surface temperature of gold nanorods. The theoretical model provides a self-consistent and unified understanding for both the anti-Stokes and Stokes one-photon luminescence from noble metal nanoparticles.

Conclusions

To summarize, we have experimentally investigated the one-photon luminescence from a single gold nanorod in detail. In addition to the conventional Stokes emission, a bright anti-Stokes emission has clearly been observed. It is enhanced by the LSPR of the plasmonic nanostructure. Using a low photon energy to excite the single gold nanorod, the anti-Stokes process avoids the influence of background signal due to inter-band transition. It was determined that both plasmon enhanced excitation and plasmon emission contribute to the photoluminescence process of the metallic nanostructures. Moreover, the anti-Stokes component is also modulated by the free electron distribution near the Fermi level, which can be used to extract localized temperature information of a single nanoparticle. Furthermore, a new theoretical model was applied to qualitatively explain the spectral line shape of one-photon luminescence from gold nanorods.

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