ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

Intrinsic luminescence from metal nanostructures and its applications

Weidong Zhang(张威东)[1], Te Wen(温特)[1], Yuqing Cheng(程宇清)[1], Jingyi Zhao(赵静怡)[1], Qihuang Gong(龚旗煌)[1,2], Guowei Lü(吕国伟)[1,2]

Citation: Chin. Phys. B . 2018, 27(9): 097302. **doi:** 10.1088/1674-1056/27/9/097302

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Improvement of green InGaN-based LEDs efficiency using a novel quantum well structure

Yangfeng Li(李阳锋), Yang Jiang(江洋), Junhui Die(迭俊珲), Caiwei Wang(王彩玮), Shen Yan(严珅), Ziguang Ma(马紫光), Haiyan Wu(吴海燕), Lu Wang(王禄), Haiqiang Jia(贾海强), Wenxin Wang(王文新), Hong Chen(陈弘)

Chin. Phys. B . 2017, 26(8): 087311. **doi:** 10.1088/1674-1056/26/8/087311

Carrier transport in III-V quantum-dot structures for solar cells or photodetectors

Wenqi Wang(王文奇), Lu Wang(王禄), Yang Jiang(江洋), Ziguang Ma(马紫光), Ling Sun(孙令), Jie Liu(刘洁), Qingling Sun(孙庆灵), Bin Zhao(赵斌), Wenxin Wang(王文新), Wuming Liu(刘伍明), Haiqiang Jia(贾海强), Hong Chen(陈弘)

Chin. Phys. B . 2016, 25(9): 097307. **doi:** 10.1088/1674-1056/25/9/097307

Excitonic transitions in Be-doped GaAs/AlAs multiple quantum well

Wei-Min Zheng(郑卫民), Su-Mei Li(李素梅), Wei-Yan Cong(丛伟艳), Ai-Fang Wang(王爱芳), Bin Li(李斌), Hai-Bei Huang(黄海北)

Chin. Phys. B . 2016, 25(4): 047302. **doi:** 10.1088/1674-1056/25/4/047302

Rectification and electroluminescence of nanostructured GaN/Si heterojunction based on silicon nanoporous pillar array

Wang Xiao-Bo, Li Yong, Yan Ling-Ling, Li Xin-Jian

Chin. Phys. B . 2015, 24(10): 107304. **doi:** 10.1088/1674-1056/24/10/107304

Investigation of the mode splitting induced by electro-optic birefringence in a vertical-cavity surface-emitting laser by polarized electroluminescence

Zhang Jie, Yu Jin-Ling, Cheng Shu-Ying, Lai Yun-Feng, Chen Yong-Hai

Chin. Phys. B . 2014, 23(2): 027304. **doi:** 10.1088/1674-1056/23/2/027304

TOPICAL REVIEW — Nanophotonics

Intrinsic luminescence from metal nanostructures and its applications

Weidong Zhang(张威东)[1], Te Wen(温特)[1], Yuqing Cheng(程宇清)[1], Jingyi Zhao(赵静怡)[1], Qihuang Gong(龚旗煌)[1,2], and Guowei Lü(吕国伟)[1,2,†]

[1] State Key Laboratory for Mesoscopic Physics & Collaborative Innovation Center of Quantum Matter, Department of Physics, Peking University, Beijing 100871, China

[2] Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China

(Received 17 April 2018; revised manuscript received 6 June 2018; published online 10 August 2018)

Intrinsic luminescence from metal nanostructures complements conventional scattering and absorption behaviors and has many interesting and unique features. This phenomenon has attracted considerable research attention in recent years because of its various potential applications. In this review, we discuss recent advances in this field, summarize potential applications for this type of luminescence, and compare theoretical models to describe the phenomena. On the basis of the excitation process, the characteristic features and corresponding applications are summarized briefly in three parts, namely, continuous-wave light, pulsed laser, and electron excitation. A universal physical mechanism likely operates in all these emission processes regardless of differences in the excitation processes; however, there remains some debate surrounding the details of the theoretical model. Further insight into these luminescence phenomena will not only provide a deeper fundamental understanding of plasmonic nanostructures but will also advance and extend their applications.

Keywords: metal nanostructure, luminescence, surface plasmon, spectroscopy

PACS: 73.20.Mf, 78.67.Bf, 78.60.Hk **DOI:** 10.1088/1674-1056/27/9/097302

1. Introduction

Metal nanostructures have enabled rapid advances in numerous interdisciplinary fields such as plasmon enhanced spectroscopy, solar energy conversion, integrated optical nanocircuitry, biosensing, and plasmonic catalysis.[1–4] All of these distinctive optical properties arise from the localized surface plasmon (LSP) resonance associated with the collective oscillations of free electrons. These features lead to unique optical properties and enable manipulation of light on a nanoscale. Notable features include localized concentration and enhancement of electromagnetic fields, LSP modes that can be tuned by size, shape, and dielectric constant of the surrounding medium, and even the coupling of LSP modes with themselves to yield Fano resonance and plasmonic metamaterials.[5]

To date, most experimental methods used to investigate singlemetal nanostructures have been based on optical scattering or absorption.[6] For example, the scattering of surface plasmons has been applied to studies of the antenna characteristics of individual and coupled gold nanoparticles.[7] Furthermore, optical absorbance and photothermal imaging have been used to determine the orientation of metal nanostructures.[8] In addition to these features, metallic materials present an intrinsic luminescence which was first reported in 1969 for bulk gold materials and then later on for rough thin films.[9–11] However, the quantum yield of this luminescence is low with an efficiency of approximately 10^{-10}. Recently, the one-photon luminescence (OPL) efficiency of gold nanorods was found to be in the order of 10^{-6}.[12] Although this quantum yield was low, the light emission process was compensated for by the large excitation cross-section of plasmonic nanostructures, thus leading to a large number of emitted photons; hence, this type of fluorescence can appear brighter than single organic fluorophores or semiconducting quantum dots.

The intrinsic photoluminescence generated from metals does not undergo photobleaching or photoblinking and enables stable observations of the spatial distribution of the emitted field of a single antenna.[13,14] Characterizing plasmonic nanostructures from their intrinsic luminescence provides an alternative flexible and simplified optical method complementary to conventional scattering and absorption techniques. The luminescence of metal nanostructures has attracted considerable interest because of its potential applications in optical recording,[15] bioimaging tags,[16,17] biosensing,[18] orientation probes,[19] local temperature detection,[20] and plasmonic resonant mode identification.[21] In addition, these phenomena are related to the broad continuum background in surface-enhanced Raman scattering[22,23] and surfaceenhanced fluorescence.[24]

A deeper understanding of this process would be helpful for understanding and optimizing plasmon enhanced spectroscopy.[25] However, there remains some controversy concerning the physical mechanism of this effect. Here, we tentatively call this luminescence process photoluminescence (PL). This process was first understood based on interband transitions. Taking gold as an example, a photon excites electrons from the d-band to the sp-band. Then, electrons in the sp-band relax to sp-electronic states near the Fermi level as

†Corresponding author. E-mail: guowei.lu@pku.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd

shown in the inset of Fig. 1(a). At the same time, holes relax to the same k point. Electron thermalization occurs over 100 fs to 1 ps.[26] The electrons finally recombine with holes to emit photons.[27] Briefly, when a metal material is illuminated by light with an energy higher than that of the interband transition, electrons relax and emit photons as shown in Fig. 1(a).

In addition to the electronic band structure, surface plasmon resonance is another important factor that influences luminescence processes, particularly in nanostructured metals. Metals possess a negative real and small positive imaginary dielectric constant that enables metals to support surface plasmons, i.e., collective oscillation of free electrons.[28] Figures 1(b) and 1(d) show two kinds of collective oscillations for a metal film and metal nanoparticle. Figures 1(a) and 1(c) show corresponding representative photoluminescence spectra. There is a strong electric field at the interface of the metal and the dielectric because of surface plasmon resonance. The high density of optical states caused by surface plasmons enhances the rates of both light absorption and emission.

A variety of different metals and nanostructures have been extensively studied including gold, silver,[29] aluminum, and copper.[10] These materials have been formed into various types of nanoscale structures with different sizes and shapes and in various coupling configurations.[30,31] In this review, most of the examples discussed concern gold nanostructures and have been widely investigated because of their ambient stability and accessibility. Notably, the same physical mechanism should also operate in other materials supporting the oscillation of free carriers. Here, we review recent advances concerning the luminescence of metal nanostructures excited by continuous wave (CW) light, pulsed lasers, and electrons together with potential applications of this luminescence. The physical origin of the luminescence is also discussed.

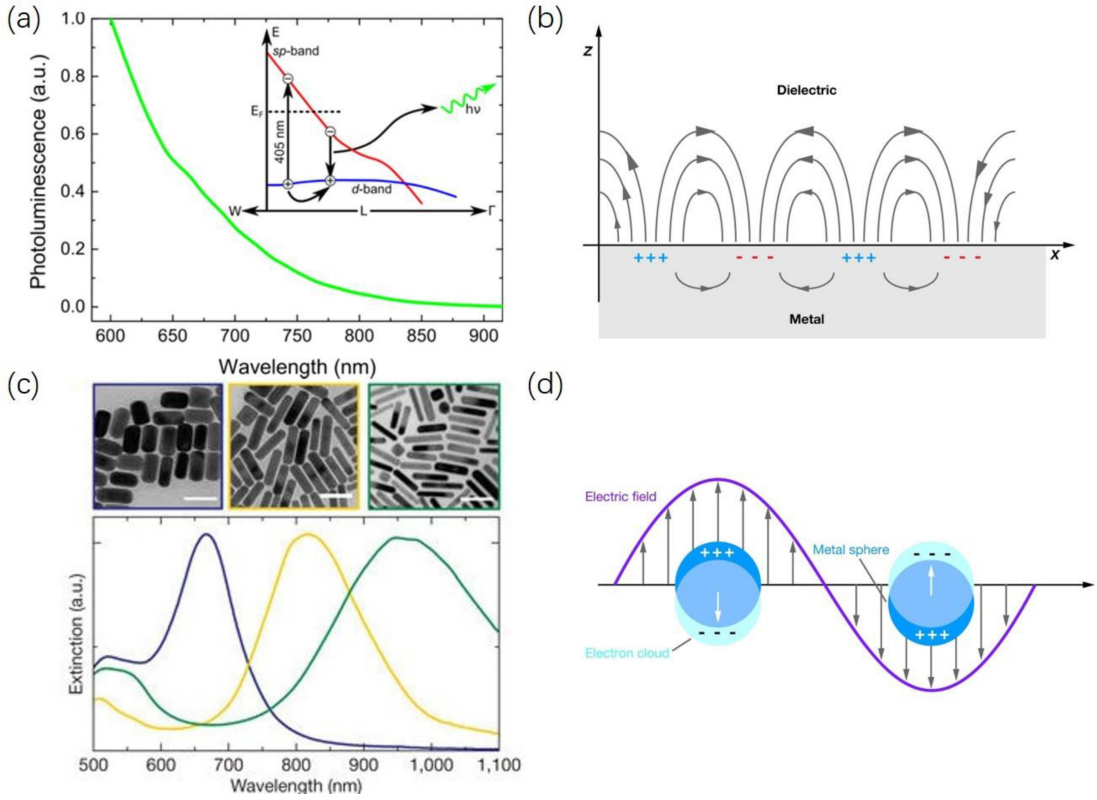


Fig. 1. (color online) (a) PL of bulk gold. Experimental OPL spectrum of gold thin film excited at 405 nm. The inset shows that OPL from bulk gold evolves by a three-step process: a d-band hole is created by 405-nm excitation and scattered within the d-band to a state below the filled sp-band states. The hole subsequently recombines radiatively with an sp-electron (from Ref. [27], Fig. 1). (b) Schematic diagram illustrating surface plasmon polariton (from Ref. [28], Fig. 1(a)). (c) Normalized extinction spectra of as-prepared gold nanorod solutions. Insets show transmission electron microscope images of gold nanorods on a copper grid. The average approximate sizes of nanorods are, from left to right, 37×19 nm, 50×12 nm, and 50×8 nm. Scale bars are 50 nm (from Ref. [15], Fig. 2(b)). (d) Schematic diagram illustrating localized surface plasmon (from Ref. [28], Fig. 1(b)).

2. Luminescence of metal nanostructures excited by CW light

Photoluminescence is weak luminescence from metal nanostructures. Here, any secondary light emission at energies different from the excitation laser energy are defined as intrinsic luminescence. When the power-law exponent of the emission intensity as a function of the excitation power is equal to 1, this luminescence can be called OPL. OPL usually takes place after excitation by CW light. OPL from bulk gold excited by CW light was first reported by Mooradian in 1969.[9] Later, gold thin films with rough surfaces were found to possess considerably higher emission efficiency compared

with that of bulk gold by Boyd *et al.* in 1986.[10] The effects of LSP on rough surface protrusions has been proposed to explain light emission enhancement. In 2000, Mohamed *et al.* showed that gold nanorods capped with micelles fluoresced with a quantum yield more than six orders of magnitude higher than that of bulk metals.[12] The OPL spectrum of gold nanoparticles always closely follows the plasmon resonance band of a particle. Such a spectral coincidence can be tuned from the visible to the infrared in gold nanorods or gap plasmons.[32,33] The LSP together with the lightning-rod effect have been used to explain the enormous enhancement of interband transitions through local field enhancement. Following these investigations, the OPL of metal nanoparticles has attracted attention because of its many potential applications. Nanostructures such as nanorods, nanoparticles,[34] nanoflowers, nanocubes,[35,36] core-shell structures,[37] and dimers,[31,38] have been prepared by chemical and lithographical methods,[33] and their OPL properties had been extensively investigated.

The shape of the OPL Stokes spectrum resembles dark field scattering when the OPL spectrum is compared with the dark field scattering spectrum of single nanostructures.[32] Slight spectral differences between OPL and scattering have been observed in previous reports.[19,32,39] Recent studies have attributed these differences to the thermalization of excited electrons to form a broad and inhomogeneous population distribution in the conduction band.[29,38] The difference becomes large when the nanostructures possess multiple or broad LSP modes.[40] Yin *et al.* designed a special nanostructure to obtain a blue-shifted OPL spectrum by controlling the polarization of the excited light.[41] Moreover, there were clear differences between the OPL anti-Stokes spectrum and scattering. These differences are likely associated with the distribution of electrons. Various line shapes have been discussed based on Bose–Einstein-like and Fermi–Dirac-like distributions.[42] The OPL Stokes spectral shape can be fitted by a Lorentz line shape. Numerical simulations and experimental studies have shown that the peak of the Lorentz line varies with the refractive index. A linear relationship exists between the peak wavelength and refractive index as shown in Fig. 2(a) which suggests potential for applications in sensing.[18,43] Furthermore, for some asymmetric nanoparticles such as gold nanoflowers, different incident-light polarization leads to different OPL emission patterns.[40] The polarization dependence of the OPL spectra has potential applications in the configuration determination of plasmonic nanostructures.

Anti-Stokes emission processes have seldom been discussed in previous studies. Anti-Stokes emission was reported by Mooradian in 1969[9] but was regarded as an emission tail on the high-energy side of a laser attributed to the thermal smearing of the electron and hole distributions. This anti-Stokes emission was considered by Neupane *et al.* to be an up-converted luminescence process in 2013.[44] Anti-Stokes emission can be enhanced by over three orders of magnitude compared with that of bulk gold when nanoparticles are excited at LSP resonances. He *et al.* claimed that electron occupation follows the Fermi–Dirac distribution and the profile of the anti-Stokes emission can in principle be applied to probe the local temperature.[20,42] Figure 2(b) shows that the temperature can be extracted by fitting the OPL anti-Stoke line shape of a single gold nanorod because the temperature controls the distribution of the electrons near the Fermi level according to Boltzmann statistics. Aquiles *et al.* showed that the anti-Stokes emission of gold nanorods can be used for imaging applications under biologically relevant conditions.[45] Gold nanorods are better than fluorescent organic dyes because of their lack of photobleaching effects. Furthermore, nanorods have a large absorption cross-section that enables bright nanoscale probing despite the low photoluminescence quantum yield of nanorods.[46]

Surface plasmons have been widely applied to enhance molecular fluorescence and Raman scattering because of the strong localized electric field around plasmonic nanostructures.[22,47–50] Light emission from nanostructured metals can be correlated with the broad background continuum in plasmon enhanced spectroscopy.[22] Quantitative correlations between the photoluminescence of metals and the SERS background are helpful for recovering native chemical information from surface-enhanced Raman scattering spectrum.[23] These spectral features contain information on the enhanced absorption and enhanced emission rate of quantum emitters. When placing an emitter around a plasmonic nanostructure, the luminescence of the metal nanostructure is enhanced. Zhao *et al.* demonstrated that gold nanoparticles coupled with fluorescent nanodiamonds mutually enhanced their light emission in experimental and theoretical investigations.[24] Figure 2(c) shows the corresponding plasmon enhanced spectra. Similarly, Raman scattering can be enhanced by placing Raman molecules around gold nanoparticles. The mechanism of this background enhancement remains unclear despite extensive investigations over the last 35 years. In recent research, Cheng *et al.* developed a theoretical model to calculate the background of enhancement.[47] Within the model, the molecule was simplified as a three-level system in the Λ configuration and the nanoparticle was simplified as a plasmonic nanostructure.[47] These findings contribute to a deeper understanding and suggest that plasmonic nanostructures and molecules are a hybrid entity for analyzing and optimizing surfaceenhanced spectroscopy.

To understand the process of OPL, the dynamics of OPL emission have also been investigated.[51–53] Varnavski *et al.* measured the decay time to be approximately 50 fs by an up-

conversion technique.[54] Hwang *et al.* reported a decay time of approximately 1–10 ps, which agreed with the results of previous reports. The decay time of metal OPL is considerably faster than that of conventional dynamic fluorescence processes in molecules or semiconductors. A fast dynamic process can be used to extract the instrument response function during lifetime measurements because the decay time is usually shorter than the instrument response time as shown in Fig. 2(d).[51] For example, Lu *et al.* used the fast luminescence of gold nanoparticles to calibrate their instrument response function during measurements of the lifetime of dye molecule photoluminescence enhanced with a bowtie nanoaperture.[52]

Optical probes play an important role in biological mechanisms and soft matter systems. Single fluorescent molecules are widely used as probes. Although single molecules have a high photoluminescence quantum yield, these chromophores are affected by blinking and bleaching. Therefore, gold nanoparticles might replace single molecules because such nanoparticles do not show blinking or bleaching. However, nanoparticles feature a low photoluminescence quantum yield despite their large absorption cross section. Boyd *et al.* studied the OPL of gold and showed that the quantum yield could be enhanced. Yorulmaz *et al.* achieved a quantum yield of approximately 10^{-6} by photothermal microscopy. After reshaping gold nanorods into nanospheres by melting, they found that the nanoparticles' quantum yield was related to their shape and resonance energy. Wilcoxin *et al.* obtained a quantum yield of approximately 10^{-5} for 5-nm gold nanospheres.[32] Mohammed *et al.* obtained a quantum yield of approximately 10^{-4} for gold nanorods. Recently, Park *et al.* found that plasmonic cube-in-cube nanoparticles with a controllable interior nanogap resulted in enhanced OPL intensity and a high quantum yield of approximately 10^{-3}.[36] The photoluminescence quantum yields of those gold nanostructures essentially depended on the excitation wavelength.[30] These studies have shown the great potential for applications of this type of luminescence for studying biological mechanisms and soft matter systems.

Nanoparticles applied in biological sensing and imaging can be affected by dynamic processes such as the mobility and aggregation of nanoparticles in a cell. The motion of nanoparticles is typically observed by dark field scattering or absorption spectroscopy. Tcherniak *et al.* studied the OPL of gold

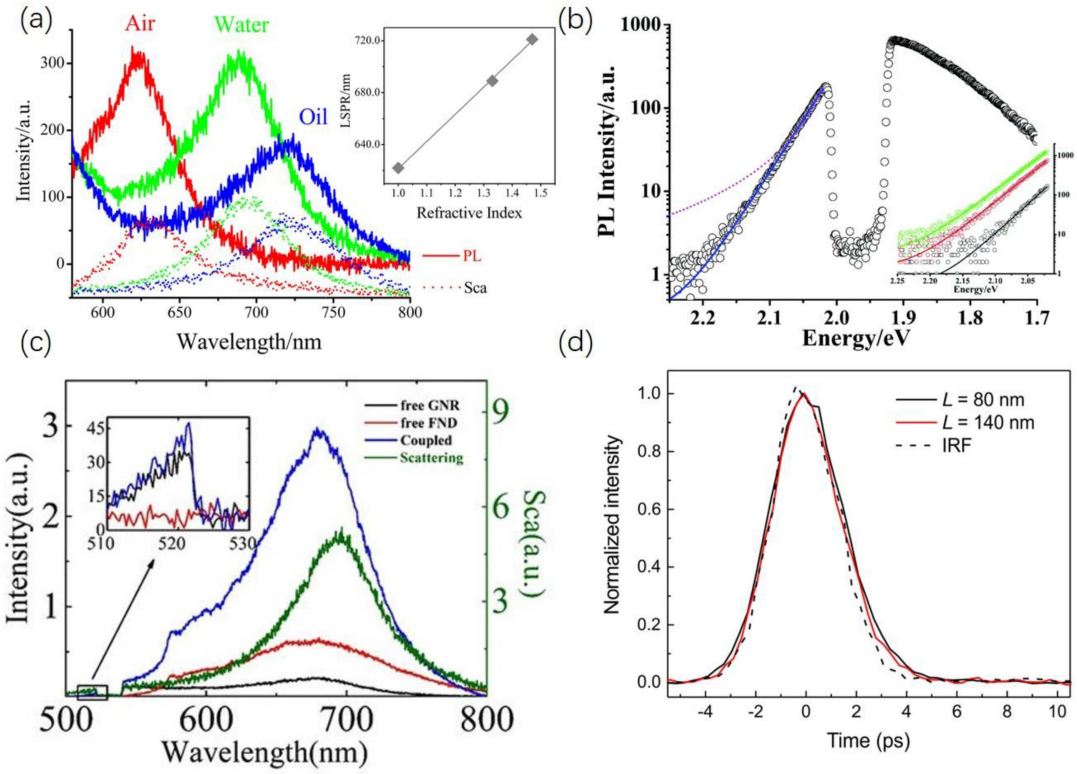


Fig. 2. (color online) (a) PL (solid lines) and scattering (dots) of a gold nanorod in different media. (Inset) LSP peak of nanorods in different media and fitting line (from Ref. [18], Fig. 2). (b) Anti-Stokes emission as a function of photon energy. Data are respectively fitted (lines) by a Boltzmann statistics distribution (blue solid line) and Lorentz line shape (purple dashed line) for the anti-Stokes part only. The inset shows the anti-Stokes spectra at different illumination light intensities with corresponding fitting lines (from Ref. [20], Fig. 3). (c) A complete analysis of three components of plasmon-enhanced fluorescence spectrum and coupling-configuration dependent spectra. OPL spectra of free single gold nanorod (black) and free single fluorescent nanodiamond (red) before coupling, plasmon-enhanced spectrum (blue), and scattering spectrum (green) after coupling of a single gold nanorod and a single fluorescent nanodiamond (from Ref. [24], Fig. 2 (a)). (d) Decay dynamics of multiphoton photoluminescence for antenna arrays of $L = 140$ nm (red curves) and $L = 80$ nm (black curves). The instrument response function (IRF) is traced with a black dashed line (from Ref. [51], Fig. 3(c)).

nanorods under different excitation polarizations.[55] The intensity of the OPL correlated with the angle between the nanorod and the light polarization. Hence, this approach enabled measurement of the orientation of a nanorod. They were able to measure the rotational diffusion constant of gold nanorods in aqueous solutions. Furthermore, the polarization of the excitation light absorption and the farfield angular distribution of OPL also depended on the orientation of the nanostructures. Zhang *et al.* measured the OPL of a single gold bipyramid, and their results showed that the OPL emission pattern was related to the orientation of the gold bipyramids.[19] After melting their gold bipyramids into nanoparticles, they showed that the emission pattern was related to the shape of the nanoparticles. Hence, orientation also can be measured through the farfield emission pattern. These studies demonstrate the potential applications of nanoparticles as dynamic probes of polarization and orientation in sensing and imaging.

Now we discuss the physical origin of OPL. For OPL from bulk metals, the shape of the spectrum does not depend on the excitation wavelength. Hence, the origin of this luminescence was first attributed to interband transitions,[9,10] i.e., radiative recombination between electrons in the conduction sp band and holes in the valence d bands. In terms of the electronic energy band structure of gold materials, the energy separation between the d-band holes and the Fermi surface is roughly 1.8 eV near the X point and 2.4 eV near the L point. Thus, when a 785-nm laser (1.58 eV) is used to excite gold nanostructures, interband transitions cannot be excited.[56] Moreover, gold nanorods have been used to study OPL because their LSP resonance can be widely tuned to the near infrared, except for regions of overlap with interband transitions.[39] However, strong infrared emission remains when the photon energy of a CW excitation laser is tuned to the infrared, for example, at 1.58 eV, which is less than the interband energy gap. Controversy remains about the physical origin of OPL based on interband transitions. Beversluis *et al.* attributed intraband transitions to infrared OPL, which is strongly mediated by LSP modes rather than interband transitions.[56,57] Alternatively, possible contributions of interband luminescence can be excluded using silver-based material systems because their interband transitions occur at up to 3.9 eV.[29,57] Suppression of interband transitions can reduce the plasmon dephasing rate.[58] Recent transient studies of visible photoluminescence have shown that the photoluminescence decay is faster than 50 fs and intraband excitations of surface plasmons provide additional contributions to interband transitions.[59]

In addition, the OPL spectral shape coincidence of metal nanostructures confirms a strong correlation between OPL and their LSP resonances. A microscopic mechanism based on the radiative decay of surface plasmons has been proposed to explain orders of magnitude increases of the luminescence quantum yield.[60] In this model, photon excited hot electron–hole pairs recombine nonradiatively. The excitation energy is then transferred to the plasmon, and radiative decay of the excited plasmon yields luminescence. This spectral coincidence has been verified from the Stoke emission of nanoparticles excited by a laser at a wavelength much shorter than the LSP resonance wavelength. Mechanisms involving interband and intraband transitions cannot sufficiently explain ultrafast processes, their dipole transition forbidden nature, or conservation of momentum. An electronic Raman scattering mechanism was proposed to match the free electron dispersion and ultrafast speed of transitions.[61–64] Several recent studies have suggested that the breakdown of symmetry in nanostructures, i.e., phonon coupling and Landau damping, allows sufficient momentum change for intraband transitions.[27,29,56] In particular, spectrally resolved nonlinear analysis of metal luminescence tends to suggest that intraband transitions are more compatible with the observed photoluminescence exponent of nonlinearity.[65] In addition, it has recently been proposed that light emission has a universal nature and the same mechanism operates across the entire spectrum based on hot-electron intraband luminescence.[57] Moreover, we have found that the OPL process is related to both the sp-band free electron distribution and localized surface plasmon resonance. Thus, we developed a phenomenological theoretical model based on a quantized optical cavity concept to simulate interactions of an electromagnetic field and a plasmonic nanoresonator.[20,66] An understanding based on the resonator concept provides an intuitive alternative way of describing these phenomena simply and quantitatively. This model helps us understand the excitation wavelengthdependent photoluminescence quantum yield of gold nanoparticles.[30] By correlating a two-temperature model and electron distributions, we demonstrated that both OPL and two-photon luminescence (TPL) from metal nanostructures involve the same mechanism.[67] To date, the physical mechanism of light emission from plasmonic nanostructures has been the subject of debate, and quantitative models of this phenomenon have yet to be developed.

3. Luminescence of metal nanostructures excited by pulsed lasers

Intense anti-Stokes broadband luminescence of metal nanostructures can be observed under pulsed-laser illumination.[68,69] When the power-law exponent of emission intensity as a function of excitation power is equal to or greater than 2, the luminescence phenomena can involve a two-photon or multiple photon process.[70,71] For simplicity, only TPL is mentioned and discussed in the following. Similar to OPL, the exact physical process of TPL is still under debate. The actual mechanism of TPL might not be related to

two-photon absorption excitation as initially believed.[61] Luminescence excited by a CW laser might also involve TPL.[72] For simplicity, we use the term TPL to describe the luminescence process occurring after pulse-laser excitation.

The TPL of metal nanostructures has many interesting properties and potential applications.[16,17,73] The quantum efficiency of OPL can be enhanced by a factor of one million owing to the LSP effect. In the same way, TPL is also considerably enhanced compared with that of bulk materials. In general, metal nanoparticles are a good choice for biological imaging. The absorption of water and biological molecules is low in the near-infrared band. Although fluorescent semiconducting quantum dots have good nonlinear characteristics, these materials are often toxic. Hence, the TPL of gold nanoparticles has potential applications in the nonlinear optical imaging of biological samples. For example, Wang *et al.* applied an 830-nm laser to excite TPL in nanorods and obtained in vivo scans. Figure 3(a) shows images of nanorods in mouse ear blood vessels. There is potential for these materials to be used in detecting cancers and in biological tagging.

Furthermore, because of the important role of LSP resonance in the TPL process, we are able to connect the spatial distribution intensity of TPL with the LSP mode.[21,74] Ghenuche *et al.* systematically studied the TPL of gold nanoantennas. Their results showed that the TPL signal spatial distribution agreed with the convoluted distribution of the fourth power of the local electric field calculated by numerical simulations. Hence, with the use of a scanning near-field microscope, plasmon modes of the nanorods were distinguished by TPL imaging. Imura *et al.* presented near-field images of nanorods of different sizes by TPL imaging.[74] The dotted line in Fig. 3(b) shows the shape of the nanorod, and the broadened image was attributed to the near-field probe tip. Nanorods of different sizes supporting different LSP modes are indicated by different spatial distributions in the TPL imaging.[75]

For LSP resonances involved in the TPL process, light absorption is polarization dependent for excited laser pulses and sensitive to the wavelength of the excited laser pulse. Owing to these features, Zijlstra *et al.* demonstrated a five-dimensional optical recording which contained information on the wavelength and polarization of an excited laser pulse and three spatial degrees of freedom.[15] The photothermal effect can also be applied to reshape nanorods to enable the recording of information.[19] Data can be recorded in three-dimensional space because photothermal melting occurs within a focal volume. Figure 3(c) shows the recording process and the high-density recording device. The TPL process also enabled read out of the data because TPL is sensitive to the polarization and wavelength of light. This work suggests the potential for applications of TPL in metal nanostructure memory devices.

A theoretical understanding of the TPL of metal nanostructures was first based on interband transitions which operate by a mechanism similar to that of the OPL process, except for the involvement of two- or multiple-photon absorption processes.[76–79] Recent work has proposed the universal nature of light emission and considered the same mechanism to operate across the entire spectrum.[57] Work by Huang *et al.* presented an alternate description of TPL as a resonant electronic Raman scattering process.[61] A new understanding of the resonator concept has provided an alternative description of both OPL and TPL phenomena simply and quantitatively.[80] In fact, oscillator models combined with a temperature dependent Fermi–Dirac distribution[26,81,82] provide a unified understanding of OPL and TPL processes.[80] The decay of excited electrons after photon excitation can be considered as a photoelectric effect or thermionic emission because laser pulses heat the electrons of the metal. We can measure a large thermionic emission and small photoelectric effect. A laser pulse can heat electrons to several thousand degrees instantaneously because the pulse duration is so short that the energy of the electrons cannot be transferred to the lattice.[26,81,82] Agranat *et al.* calculated the intensity of the emission, and these results provided support for thermionic

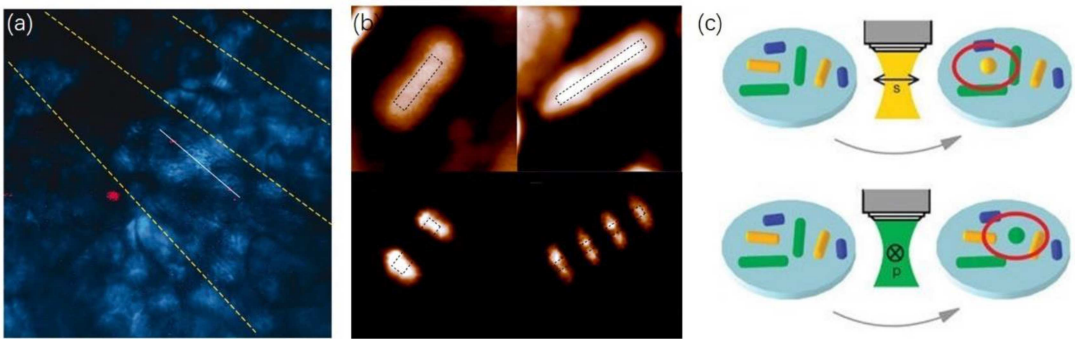


Fig. 3. (color online) (a) *In vivo* imaging of single gold nanorods in mouse ear blood vessels. Overlay of transmission image (light blue) and single-frame TPL image. Two single nanorods (red spots) superimposed by a line scan (white). Image size is 175 μm × 175 μm (from Ref. [16], Fig. 5(c)). (b) Topographic images of gold nanorods and two-photon-induced photoluminescence images of gold nanorods (from Ref. [74], Fig. 2)). (c) The process of reshaping gold nanorods in the focal volume of focusing objective. Some nanorods that couple with light can be reshaped for optical recording (from Ref. [15], Fig. 2(a)).

emission.[68,69] The features of the phenomenon might be useful for studying the relaxation kinetics of electrons and the lattice and the noninertial conversion of picosecond IR laser pulses into visible light. Although the resonator concept provides a general and intuitive model for understanding intrinsic light emission phenomena of metallic nanostructures, a complete microscopic model has yet to be determined. The electronic band structure, dynamic processes of electron and hole distribution, interactions of electrons and phonons, and coupling between plasmon modes should also be considered.[83–85]

4. Luminescence of metal nanostructures excited by electrons

In addition to photon excitation, intrinsic luminescence of metal nanostructures also occurs under electron excitation such as cathodoluminescence (CL) in electron microscopes, tunneling electrons through the probe apex in scanning tunneling microscopes, and tunneling electrons within the nano-gap of electrodes. These excitation processes are very different; however, the shapes of emission spectra of gold nanostructures show a strong correlation with their LSP modes. Hence, there should be a common physical mechanism operating for these emission processes regardless of the excitation process. This correlation might be helpful for determining the physical mechanism of luminescence of metal nanostructures. In terms of the high similarity of the emission features for different excitation processes, an understanding of the luminescence process based on an oscillator model could provide a unified model.[80] Here, we briefly review three ways of electronic excitation that can generate luminescence of metal nanostructures.

At first, electron microscopy involves several kinds of processes depending on the signal collection mode, such as CL, secondary electron, and electron energy inelastic losses. When metallic nanoparticles (e.g., silver particles[86] or gold nanoclusters[87]) are exposed to fast electron beams, the localized plasmon mode can be excited and decay radiatively and contribute to light emission.[88,89] Electrons also excite e-h pairs of semiconductors (or molecules) which decay radiatively and contribute to the luminescence. Here, CL is restricted to luminescence from metal nanostructures after electron beam excitation in electron microscopy. We will not review the mechanism of CL since several comprehensive review articles already exist on this subject.[88] CL techniques can be used for imaging at the spatial resolution of the LSP modes because of the high-spatial resolution of electrons compared with that of visible light. For instance, Atre *et al.* applied CL tomography to image metal structures in three dimensions on a nanoscale. They demonstrated CL reconstruction imaging of a three-dimensional metaldielectric crescent. Vesseur *et al.* imaged a nanowire by CL image spectroscopy. Figure 4(a) shows the plasmon behavior and the eigenmodes with distinct spatial profiles of gold nanowire.[90,91] Coenen *et al.* studied the spectral and angular CL patterns of nanoholes. They also showed a directional emission of a linear array of Au nanoparticles by angle-resolved CL spectroscopy when a high-energy electron beam irradiated the first Au nanoparticle.[92]

For the tunneling-electron induced luminescence of metals, luminescence from metal-oxide-metal sandwich junctions (Au or Ag) has been studied and discussed.[93] However, a theoretical explanation of this phenomenon has yet to be agreed on. It is not clear how inelastic electron tunneling or hot electron excitation of radiative plasmon modes contribute to the emission. When fluorescent molecules are introduced between a metal tip and substrate, the luminescence process becomes more complex.[94] Tunneling electrons can excite plasmonic nano-cavities, and the cavity can excite the electrons of molecules to higher vibrational states. The higher vibrational states are induced by a plasmon-assisted multistep inelastic scattering scheme. For simplicity, Kravtsov *et al.* measured light emission from a tip-film gap structure at different distances.[95] The peak energy of the luminescence correlated with the distance, which indicated that the luminescence was from plasmon resonance rather than tunneling electrons because they used a low bias voltage. Le Moal *et al.* used a similar method to investigate light emission by changing the position of the tip with respect to the gold nanoparticle as shown in Fig. 4(b).[96] They demonstrated that inelastic electron tunneling between the tip and gold nanoparticle can result in directional emission, which is related to the interference of the LSP modes.

It has already been shown that visible light can be generated through electron tunneling. Lambe *et al.* discovered broadband light emission when applying a voltage to a metal-insulator-metal tunneling junction.[97] The emission with a high-frequency linear cutoff can be described by the expression $L(\upsilon) = P(\nu, V)(|V| - h\nu/e)\theta(|V| - h\nu/e)$. Here, $P(\nu, V)$ is a packaging function and $\theta(x)$ is a cutoff function. The luminescence process is described by two steps: (i) electrons tunnel through the insulator from occupied states to unoccupied states in the other electrode without energy loss, and (ii) these higher energy electrons are thermalized. In this process, the surface plasmon modes in the tunnel junction can enhance inelastic tunneling. Parzefall *et al.* performed a control experiment to show that surface plasmon modes can enhance emission and that the cutoff voltage influences the emission spectrum.[98] Furthermore, Kern *et al.* assembled a gold nanoparticle between two electrodes to form an electrically driven optical antenna, as shown in Fig. 4(c).[99,100] Gurunarayanan *et al.* placed an antenna in a V-electrode and achieved broadband unidirectional emission owing to the enhancement of the dipolar emission at the tunnel junction and the fundamental quadrupole-like resonance of the antenna.[101] Ward *et al.* used a typical nanogap con-

sisting of two gold nanojunctions to demonstrate surface-enhanced Raman scattering.[102] Dathe *et al.* used a similar structure in label-free detection of small biomolecules. When biomolecules were adsorbed around the nanoparticles, the peak of the emission spectral shifted.[103] The luminescence of metal nanostructures caused by the tunneling electric current includes various interesting phenomena. Applications of these materials include biosensing, high-frequency modulation, and basic components for transmission and reflection spectroscopy.

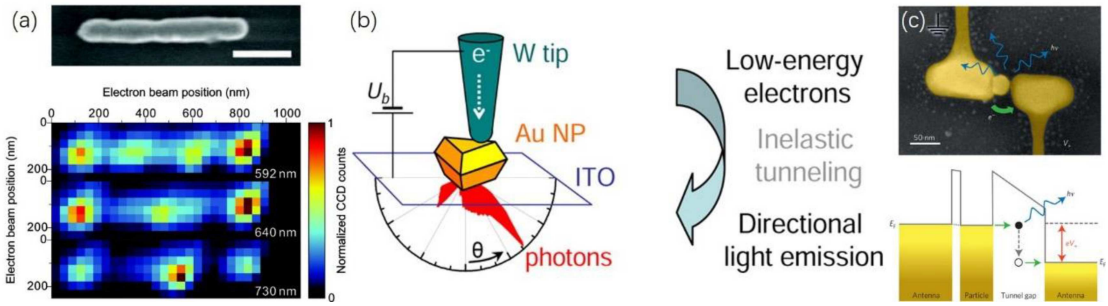


Fig. 4. (color online) (a) Upper part: SEM image of 725nmlong Au nanowire on Si substrate (scale bar is 250 nm). Lower part: CL images measured at wavelengths of 592, 640, and 730 nm from the nanowire (from Ref. [90], Fig. 1). (b) Left: schematic of experiment. Angular distribution of emission occurs when the tip is moved to a different position on the gold nanoparticle. Right: Energy transfer schematic of Ref. [96]. (c) Electron microscope image of lateral tunnel structure: electrically connected single crystalline gold nanoantenna loaded with coated gold nanoparticles on glass substrate ($V+$: applied voltage; e^-: electron flow; $h\nu$: light emission). Second: tunnel gap with applied voltage (EF, Fermi energy, and electrochemical potential of Ref. [99], Fig. 1).

5. Conclusion and perspectives

In this review, we discussed several aspects of the most exciting and promising research directions in the field of intrinsic luminescence of metal nanostructures. Surface plasmons can be excited by CW light, pulsed lasers, electron beams, or tunneling electric current. Then, the plasmon decays radiatively resulting in luminescence for various applications. This luminescence can be excited in other ways, such as by chemical reactions[104] or by highenergy photons. For example, the luminescence of gold nanoparticles induced by X-rays has been reported.[105] The physical mechanism has yet to be confirmed in this research field. Although many theoretical models have been proposed to explain these phenomena, there is a lack of a theoretical consensus in this field. Owing to the losses of the metal, the quantum yields of this luminescence are low, which limits its applications. Hence, efforts are still needed to further improve the quantum yield of intrinsic luminescence from plasmonic nanostructures. Since there is a strong correlation between surface plasmon modes and luminescence features which can be controlled through the shape, size, and coupling configuration of the nanomaterial, optimizing these properties could improve luminescence for various functions and different devices. A considerable scope remains for exploring potential applications based on metal luminescence.

References

[1] Moskovits M 1985 *Rev. Mod. Phys.* **57** 783
[2] Anker J N, Hall W P, Lyandres O, Shah N C, Zhao J and Van Duyne R P 2008 *Nat. Mater.* **7** 442
[3] Baffou G and Quidant R 2014 *Chem. Soc. Rev.* **43** 3898
[4] Brongersma M L, Halas N J and Nordlander P 2015 *Nat. Nanotechnol.* **10** 25
[5] Monticone F and Alu A 2014 *Chin. Phys. B* **23** 047809
[6] Crut A, Maioli P, Del Fatti N and Vallee F 2014 *Chem. Soc. Rev.* **43** 3921
[7] Shen H, Lu G, Zhang T, Liu J, Gu Y, Perriat P, Martini M, Tillement O and Gong Q 2013 *Nanotechnology* **24** 285502
[8] Chang W S, Willingham B, Slaughter L S, Dominguez-Medina S, Swanglap P and Link S 2012 *Acc. Chem. Res.* **45** 1936
[9] Mooradian A 1969 *Phys. Rev. Lett.* **22** 185
[10] Boyd G T, Yu Z H and Shen Y R 1986 *Phys. Rev. B* **33** 7923
[11] Apell P, Monreal R and Lundqvist S 1988 *Phys. Scr.* **38** 174
[12] Mohamed M B, Volkov V, Link S and El-Sayed M A 2000 *Chem. Phys. Lett.* **317** 517
[13] Klar T, Perner M, Grosse S, von Plessen G, Spirkl W and Feldmann J 1998 *Phys. Rev. Lett.* **80** 4249
[14] Tcherniak A, Ha J W, Dominguez-Medina S, Slaughter L S and Link S 2010 *Nano Lett.* **10** 1398
[15] Zijlstra P, Chon J W and Gu M 2009 *Nature* **459** 410
[16] Wang H, Huff T B, Zweifel D A, He W, Low P S, Wei A and Cheng J X 2005 *Proc. Natl. Acad. Sci. USA* **102** 15752
[17] Jiang Y Q, Horimoto N N, Imura K, Okamoto H, Matsui K and Shigemoto R 2009 *Adv. Mater.* **21** 2309
[18] Lu G W, Hou L, Zhang T Y, Liu J, Shen H M, Luo C X and Gong Q H 2012 *J. Phys. Chem. C* **116** 25509
[19] Zhang T, Shen H, Lu G, Liu J, He Y, Wang Y and Gong Q 2013 *Adv. Opt. Mater.* **1** 335
[20] He Y, Xia K, Lu G, Shen H, Cheng Y, Liu Y C, Shi K, Xiao Y F and Gong Q 2015 *Nanoscale* **7** 577
[21] Ghenuche P, Cherukulappurath S, Taminiau T H, van Hulst N F and Quidant R 2008 *Phys. Rev. Lett.* **101** 116805
[22] He Y B, Lu G W, Shen H M, Cheng Y Q and Gong Q H 2015 *Appl. Phys. Lett.* **107**
[23] Lin K Q, Yi J, Zhong J H, Hu S, Liu B J, Liu J Y, Zong C, Lei Z C, Wang X, Aizpurua J, Esteban R and Ren B 2017 *Nat. Commun.* **8** 14891
[24] Zhao J Y, Cheng Y Q, Shen H M, Hui Y Y, Wen T, Chang H C, Gong Q H and Lu G W 2018 *Sci. Rep.* **8** 3605
[25] Cheng Y Q, Lu G W, shen H M, Wang Y W, He Y B, Chou R Y Y and Gong Q H 2015 *Opt. Commun.* **350** 40
[26] Sun C K, Vallée F, Acioli L H, Ippen E P and Fujimoto J G 1994 *Phys. Rev. B* **50** 15337
[27] Sivun D, Vidal C, Munkhbat B, Arnold N, Klar T A and Hrelescu C 2016 *Nano Lett.* **16** 7203
[28] Willets K A and Van Duyne R P 2007 *Annu. Rev. Phys. Chem.* **58** 267

[29] Lin K Q, Yi J, Hu S, Sun J J, Zheng J T, Wang X and Ren B 2016 *ACS Photon.* **3** 1248
[30] Cheng Y, Lu G, He Y, Shen H, Zhao J, Xia K and Gong Q 2016 *Nanoscale* **8** 2188
[31] Huang D, Byers C P, Wang L Y, Hoggard A L, Hoenee B, Dominguez-Medina S, Chen S S, Chang W S, Landes C F and Link S 2015 *ACS Nano* **9** 7072
[32] Yorulmaz M, Khatua S, Zijlstra P, Gaiduk A and Orrit M 2012 *Nano Lett.* **12** 4385
[33] Yin T, Dong Z, Jiang L, Zhang L, Hu H, Qiu C W, Yang J K W and Shen Z X 2016 *ACS Photon.* **3** 979
[34] Zheng J, Zhou C, Yu M X and Liu J B 2012 *Nanoscale* **4** 4073
[35] Park J E, Kim J and Nam J M 2017 *Chem. Sci.* **8** 4696
[36] Park J E, Kim S, Son J, Lee Y and Nam J M 2016 *Nano Lett.* **16** 7962
[37] Wang Y W, Shen H M, He Y B, Cheng Y Q, Perriat P, Martini M, Tillement O, Gong Q H and Lu G W 2014 *Chem. Phys. Lett.* **610** 278
[38] Hu H L, Duan H G, Yang J K W and Shen Z X 2012 *ACS Nano* **6** 10147
[39] Fang Y, Chang W S, Willingham B, Swanglap P, Dominguez-Medina S and Link S 2012 *ACS Nano* **6** 7177
[40] Zhang T, Lu G, Shen H, Shi K, Jiang Y, Xu D and Gong Q 2015 *Sci. Rep.* **4** 3867
[41] Yin T T, Dong Z G, Jiang L Y, Zhang L, Hu H L, Qiu C W, Yang J K W and Shen Z X 2016 *ACS Photon.* **3** 979
[42] Wen T, He Y, Liu X L, Lin M L, Cheng Y, Zhao J, Gong Q, Xia K, Tan P H and Lu G 2017 *AIP Adv.* **7** 125106
[43] He Y, Cheng Y, Zhao J, Li X Z, Gong Q and Lu G 2016 *J. Phys. Chem. C* **120** 16954
[44] Neupane B, Zhao L Y and Wang G F 2013 *Nano Lett.* **13** 4087
[45] Carattino A, Caldarola M and Orrit M 2018 *Nano Lett.* **18** 874
[46] Carattino A, Keizer V I P, Schaaf M J M and Orrit M 2016 *Biophys. J.* **111** 2492
[47] Cheng Y, Zhao J, Wen T, Li G, Xu J, Hu A, Gong Q and Lu G 2017 *J. Phys. Chem. C* **121** 23626
[48] Carles R, Bayle M, Benzo P, Benassayag G, Bonafos C, Cacciato G and Privitera V 2015 *Phys. Rev. B* **92** 174302
[49] Mahajan S, Cole R M, Speed J D, Pelfrey S H, Russell A E, Bartlett P N, Barnett S M and Baumberg J J 2010 *J. Phys. Chem. C* **114** 7242
[50] Cao Z M, He Y B, Cheng Y Q, Zhao J Y, Li G T, Gong Q H and Lu G W 2016 *Appl. Phys. Lett.* **109**
[51] Sakat E, Bargigia I, Celebrano M, Cattoni A, Collin S, Brida D, Finazzi M, D'Andrea C and Biagioni P 2016 *Acs Photon.* **3** 1489
[52] Lu G W, Li W Q, Zhang T Y, Yue S, Liu J, Hou L, Li Z and Gong Q H 2012 *ACS Nano* **6** 1438
[53] Klemm P, Haug T, Bange S and Lupton J M 2014 *Phys. Rev. Lett.* **113** 266805
[54] Varnavski O P, Goodson T, Mohamed M B and El-Sayed M A 2005 *Phys. Rev. B* **72** 235405
[55] Tcherniak A, Dominguez-Medina S, Chang W S, Swanglap P, Slaughter L S, Landes C F and Link S 2011 *J. Phys. Chem. C* **115** 15938
[56] Beversluis M R, Bouhelier A and Novotny L 2003 *Phys. Rev. B* **68** 115433
[57] Haug T, Klemm P, Bange S and Lupton J M 2015 *Phys. Rev. Lett.* **115** 067403
[58] Sonnichsen C, Franzl T, Wilk T, von Plessen G, Feldmann J, Wilson O and Mulvaney P 2002 *Phys. Rev. Lett.* **88** 077402
[59] Varnavski O P, Mohamed M B, El-Sayed M A and Goodson T 2003 *J. Phys. Chem. B* **107** 3101
[60] Dulkeith E, Niedereichholz T, Klar T A, Feldmann J, von Plessen G, Gittins D I, Mayya K S and Caruso F 2004 *Phys. Rev. B* **70** 205424
[61] Huang J, Wang W, Murphy C J and Cahill D G 2014 *Proc. Natl. Acad. Sci. USA* **111** 906
[62] Hugall J T and Baumberg J J 2015 *Nano Lett.* **15** 2600
[63] Mertens J, Kleemann M E, Chikkaraddy R, Narang P and Baumberg J J 2017 *Nano Lett.* **17** 2568
[64] Otto A, Akemann W and Pucci A 2010 *Isr J. Chem.* **46** 307
[65] Roloff L, Klemm P, Gronwald I, Huber R, Lupton J M and Bange S 2017 *Nano Lett.* **17** 7914
[66] Xia K Y, He Y B, Shen H M, Cheng Y Q, Gong Q H and Lu G W 2015 *Micro+ Nano Mater. Devices Syst.* **9668** 96685B
[67] Shahbazyan T V 2013 *Nano Lett.* **13** 194
[68] al M B A e 1980 *Sov. Phys. JETP* **52** 27
[69] Agranat M B, Benditskii A A, Gandelman G M, Devyatkov A G, Kondratenko P S, Makshantsev B I, Rukman G I and Stepanov B M 1979 *JETP Lett.* **30** 167
[70] Bouhelier A, Bachelot R, Lerondel G, Kostcheev S, Royer P and Wiederrecht G P 2005 *Phys. Rev. Lett.* **95** 267405
[71] Farrer R A, Butterfield F L, Chen V W and Fourkas J T 2005 *Nano Lett.* **5** 1139
[72] Zhang Z X, Sonek G J, Wei X B, Sun C, Berns M W and Tromberg B J 1999 *J. Biomed. Opt.* **4**

Zhanxiang Zhang; Gregory J. Sonek; Xunbin Wei; Chung-Ho Sun; Michael W. Berns; Bruce J. Tromberg
[73] Durr N J, Larson T, Smith D K, Korgel B A, Sokolov K and Ben-Yakar A 2007 *Nano Lett.* **7** 941
[74] Imura K, Nagahara T and Okamoto H 2004 *J. Am. Chem. Soc.* **126** 12730
[75] Biagioni P, Celebrano M, Savoini M, Grancini G, Brida D, Mátéfi-Tempfli S, Mátéfi-Tempfli M, Duò L, Hecht B, Cerullo G and Finazzi M 2009 *Phys. Rev. B* **80** 045411
[76] Eichelbaum M, Schmidt B E, Ibrahim H and Rademann K 2007 *Nanotechnology* **18** 355702
[77] Wang Q Q, Han J B, Guo D L, Xiao S, Han Y B, Gong H M and Zou X W 2007 *Nano Lett.* **7** 723
[78] Biagioni P, Brida D, Huang J S, Kern J, Duo L, Hecht B, Finazzi M and Cerullo G 2012 *Nano Lett.* **12** 2941
[79] Bouhelier A, Beversluis M R and Novotny L 2003 *Appl. Phys. Lett.* **83** 5041
[80] Cheng Y Q, Zhang W D, Zhao J Y, Wen T, Hu A Q, Gong Q H and Lu G W 2018 *Nanotechnology* **29**
[81] Sun C K, Vallée F, Acioli L, Ippen E P and Fujimoto J G 1993 *Phys. Rev. B* **48** 12365
[82] Groeneveld R H M, Sprik R and Lagendijk A 1995 *Phys. Rev. B* **51** 11433
[83] Sundararaman R, Narang P, Jermyn A S, Goddard W A and Atwater H A 2014 *Nat. Commun.* **5** 5788
[84] Bernardi M, Mustafa J, Neaton J B and Louie S G 2015 *Nat. Commun.* **6** 7044
[85] Brown A M, Sundararaman R, Narang P, Goddard W A, 3rd and Atwater H A 2016 *ACS Nano* **10** 957
[86] Yamamoto N, Araya K and de Abajo F J G 2001 *Phys. Rev. B* **64** 205419
[87] Yu A, Li S, Czap G and Ho W 2016 *Nano Lett.* **16** 5433
[88] de Abajo F J G 2010 *Rev. Mod. Phys.* **82** 209
[89] Atre A C, Brenny B J M, Coenen T, Garcia-Etxarri A, Polman A and Dionne J A 2015 *Nat. Nanotechnol.* **10** 429
[90] Vesseur E J R, de Waele R, Kuttge M and Polman A 2007 *Nano Lett.* **7** 2843
[91] Coenen T and Polman A 2014 *ACS Nano* **8** 7350
[92] Coenen T, Vesseur E J, Polman A and Koenderink A F 2011 *Nano Lett.* **11** 3779
[93] Berndt R, Gimzewski J K and Johansson P 1991 *Phys. Rev. Lett.* **67** 3796
[94] Dong Z C, Zhang X L, Gao H Y, Luo Y, Zhang C, Chen L G, Zhang R, Tao X, Zhang Y, Yang J L and Hou J G 2010 *Nat. Photon.* **4** 50
[95] Kravtsov V, Berweger S, Atkin J M and Raschke M B 2014 *Nano Lett.* **14** 5270
[96] Le Moal E, Marguet S, Rogez B, Mukherjee S, Dos Santos P, Boer-Duchemin E, Comtet G and Dujardin G 2013 *Nano Lett.* **13** 4198
[97] Lambe J and McCarthy S L 1976 *Phys. Rev. Lett.* **37** 923
[98] Parzefall M, Bharadwaj P, Jain A, Taniguchi T, Watanabe K and Novotny L 2015 *Nat. Nanotechnol.* **10** 1058
[99] Kern J, Kullock R, Prangsma J, Emmerling M, Kamp M and Hecht B 2015 *Nat. Photon.* **9** 582
[100] Vardi Y, Cohen-Hoshen E, Shalem G and Bar-Joseph I 2016 *Nano Lett.* **16** 748
[101] Gurunarayanan S P, Verellen N, Zharinov V S, Shirley F J, Moshchalkov V V, Heyns M, Van de Vondel J, Radu I P and Van Dorpe P 2017 *Nano Lett.* **17** 7433
[102] Ward D R, Corley D A, Tour J M and Natelson D 2011 *Nat. Nanotechnol.* **6** 33
[103] Dathe A, Ziegler M, Hubner U, Fritzsche W and Stranik O 2016 *Nano Lett.* **16** 5728
[104] Ou M G, Lu G W, Shen H, Descamps A, Marquette C A, Blum L J, Ledoux G, Roux S, Tillement O, Cheng B L and Perriat P 2007 *Adv. Funct. Mater.* **17** 1903
[105] Lee K H, Lai S F, Lin Y C, Chou W C, Ong E B L, Tan H R, Tok E S, Yang C S, Margaritondo G and Hwu Y 2014 *Mater. Chem. Phys.* **149** 582