

Strong two-photon fluorescence enhanced jointly by dipolar and quadrupolar modes of a single plasmonic nanostructure

Tianyue Zhang, Guowei Lu, Jie Liu, Hongming Shen, Pascal Perriat et al.

Citation: *Appl. Phys. Lett.* **101**, 051109 (2012); doi: 10.1063/1.4742148

View online: <http://dx.doi.org/10.1063/1.4742148>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v101/i5>

Published by the [American Institute of Physics](#).

Related Articles

Observation of intermediate bands in Eu³⁺ doped YPO₄ host: Li⁺ ion effect and blue to pink light emitter
[AIP Advances 2, 032119 \(2012\)](#)

Silver nanoclusters decked diamond thin film as a substrate for surface-enhanced Raman scattering
[AIP Advances 2, 032102 \(2012\)](#)

Radiative and non-radiative effects of a substrate on localized plasmon resonance of particles
[J. Appl. Phys. 112, 013529 \(2012\)](#)

Stimulated Mie scattering in nanocrystals suspension
[Appl. Phys. Lett. 101, 011110 \(2012\)](#)

Optical and magnetic properties of Cr-doped ZnS nanocrystallites
[J. Appl. Phys. 111, 123525 \(2012\)](#)

Additional information on *Appl. Phys. Lett.*

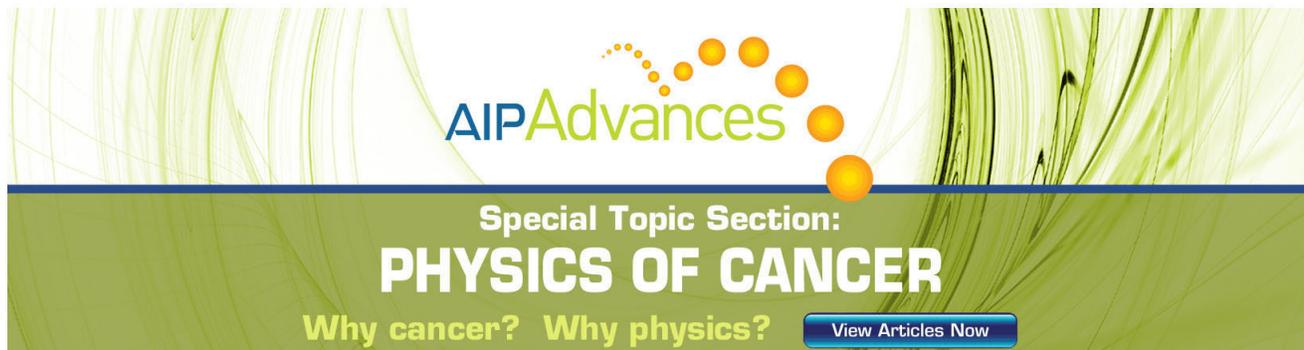
Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



AIP Advances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Strong two-photon fluorescence enhanced jointly by dipolar and quadrupolar modes of a single plasmonic nanostructure

Tianyue Zhang,¹ Guowei Lu,^{1,a)} Jie Liu,¹ Hongming Shen,¹ Pascal Perriat,² Matteo Martini,³ Olivier Tillement,³ and Qihuang Gong^{1,a)}

¹State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, Beijing 100871, China

²MATEIS, UMR 5510 CNRS, INSA-Lyon, Université de Lyon, 20 av. Albert Einstein, 69621 Villeurbanne Cedex, France

³LPCML, Université de Lyon, Université Claude Bernard, 43 Bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France

(Received 10 June 2012; accepted 18 July 2012; published online 1 August 2012)

A single gold nano-cylinder presenting multipolar plasmon resonances to enhance two-photon fluorescence is investigated employing three dimensional finite-difference time-domain method. Cylinders of large dimension usually display dipolar and quadrupolar plasmonic resonances. We demonstrate that the dipolar resonance can couple with the incident light resulting in a large localized field enhancement which increases the molecular excitation rate. At the same time, the radiative quadrupolar mode overlaps with the emission band of excited fluorophores to assist the fluorescence emission due to an enhancement in the quantum efficiency. Such dipole-quadrupole jointly enhanced two-photon fluorescence exhibits exceptionally promise in brighter label design.

© 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742148>]

Two-photon excited fluorescence has opened a rapidly expanding field of biological imaging studies during the past two decades, and it continues to find an increasing number of applications in biosensing and medicine.^{1–3} Two-photon excitation of fluorophores resulting from the simultaneous absorption of two photons has distinct advantages such as large penetration depth and reduced photodamage for the use of near-infrared light, three-dimensional confinement fluorescence excitation and high-contrast images because of the quadratic excitation intensity dependence, and high signal-to-background ratio fluorescence detection due to the broad spectral separation of the excitation light from the induced fluorescence.^{1,2} In recent years, there have been many efforts to improve the performance of two-photon excitation fluorescence (TPEF), for instance, the design of fluorescent dye probes with large two-photon absorption cross-sections.^{4,5} The more appealing scheme is so-called metal-enhanced fluorescence based on the coupling of the fluorophores and the plasmonic nanostructures, which would result in enhanced fluorescence intensity, shortened fluorescence lifetime, and extended photostability.^{6–8} Metal-enhanced fluorescence has attracted tremendous interest of researchers, and theoretical and experimental investigations were performed widely for one-photon excitation fluorescence process.⁶ In metal-enhanced fluorescence, spectral correlation between localized surface plasmon resonances (LSPR) modes of plasmonic nanostructures and fluorophores' absorption/emission spectra has been convinced to be critical by numerous studies for metallic nanoparticles, nanoscale metallic films, or ordered arrays of nanopatterns.^{8,9} The overlap of the molecule absorption spectra with plasmonic resonance can remarkably increase the excitation rates of fluorophores due to strongly enhanced local excitation field.¹⁰ On the other hand, tuning

the LSPR to the fluorophores' emission band, metallic nanostructures can change the total quantum efficiency by modifying the radiative and nonradiative decay rates.¹¹ To optimally enhance the fluorescence intensity, it is better that the plasmonic spectral features cover both fluorophores absorption and emission, which means that the linewidth of LSPR mode needs to be significantly broadened. However, broad plasmon resonance would lead to fast radiative damping which deteriorates the quality factor and the field enhancement effect and leading to low fluorescence enhancement. This is particularly true for TPEF where the Stokes shift is usually larger between the excitation and emission band. However, the surface enhanced TPEF is much underappreciated, and the systematically theoretical study of surface enhanced two-photon fluorescence has even seldom been reported.

Recently, it has been found that the higher-order multipolar resonances of plasmonic nanostructure (which are often dark modes) become to be able to couple with the free space incident electromagnetic field.^{12–14} This exciting effect allows us to utilize the multipolar mode with the dipolar mode to cooperatively enhance the molecules fluorescence in excitation and emission processes simultaneously. The dipolar resonance is proposed to couple with the free space excitation light which would result in a large enhanced localized excitation field while at the same time the quadrupolar resonance mode is tuned to overlap with the emission band of the fluorescent molecule which would improve the light emission efficiency. In this study, we demonstrate metal-enhanced two-photon fluorescence with dipolar and quadrupolar modes of a single gold cylinder nanostructure based on a single emitter-single metal structure configuration. Key parameters such as emitter's position, orientation, and spectra overlaps between molecular band and plasmon resonances are also investigated to optimize the enhancement effect.

We model the single emitter-single nanostructure system employing three-dimensional finite-difference time-domain

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: guowei.lu@pku.edu.cn and qhgong@pku.edu.cn.

(FDTD) calculations.¹⁵ An oscillating classical point dipole is considered as an isolated emitter, with a radiative decay rate Γ_{rad}^0 , nonradiative decay rate Γ_{nrad}^0 and quantum efficiency $\eta_0 = \Gamma_{rad}^0 / (\Gamma_{rad}^0 + \Gamma_{nrad}^0)$. The presence of a metallic nanostructure introduces an additional nonradiative decay channel due to metal losses. The modified radiative decay rate is now denoted as Γ_{rad} that accounts for the energy reaching the far field. When the isolated emitter is coupled to the nanoantenna, the emission efficiency changes to

$$\eta(\omega) = \eta_{0(\omega)} / [(1 - \eta_{0(\omega)}) / F(\omega) + \eta_{0(\omega)} / \eta_{a(\omega)}]. \quad (1)$$

In this relation, $F(\omega) = \Gamma_{rad} / \Gamma_{rad}^0$ is the Purcell factor, representing the enhancement of the radiative decay rate and $\eta_a(\omega) = \Gamma_{rad} / (\Gamma_{rad} + \Gamma_{nrad})$ is the antenna efficiency, which is the power that reaches the far field divided by the total emitting power. Then the TPEF signal of the isolated emitter is

$$S \propto k \cdot \sigma_{(\omega)}^{2P} \cdot \eta(\omega) \cdot |p \cdot E|^4. \quad (2)$$

Here, k is the collection efficiency (assuming the signal is collected over all angles, it is the same with or without antenna), p is the transition electric dipole moment, and E is the electric field at the emitter position. Moreover, for simplicity, the two-photon absorption cross-section of the fluorophores is supposed the same for all excitation wavelengths. Then, the TPEF brightness of the emitter studied is approximately only related to local field enhancement and the quantum efficiency. Precisely, we focus our attention on a single emitter in the vicinity of a gold cylinder placed on a silica substrate. Indeed, cylinder nanostructures can be fabricated easily and their surface plasmon resonance can be tuned by adjusting the diameter or height. Recently, it has been applied experimentally for ultrasensitive detection through metal-enhanced TPEF, while the theoretical investigation is lacking.⁸ The optical dielectric function of gold is modeled using the Drude-Lorentz dispersion model¹⁶ and the system is immersed in water. The refractive index is equal to 1.33 for water and 1.49 for silica without loss.

Recent studies have shown that higher-order resonances can be excited directly with free-space incident light due to the symmetry breaking. This permits the coupling between the dark multipolar modes with the dipolar bright mode or leads to the Fano resonances.^{13,14} Here, the plasmon resonances of the cylinder are first calculated using plane wave illumination: the results reveals that the plasmon resonances of the cylinder presents a good tunability by adjusting the diameter versus height (i.e., d/h ratio) (see supporting information²³). When the dimensions of the cylinder or d/h ratio increases beyond the quasi-static limit, quadrupolar plasmon resonance modes appear, which is due to retardation effects. As shown in Fig. 1(a), the optical absorption spectra of cylinder d70-h20 (denoting the cylinder with diameter $d = 70$ nm, height $h = 20$ nm) only presents dipolar mode, while the cylinder d150-h20 presents obvious both dipolar and quadrupolar modes. For the small size cylinder where the quasi-static approximation is valid (its dimension is much smaller than the incident wavelength), only dipolar plasmon mode can be efficiently excited by incident light.

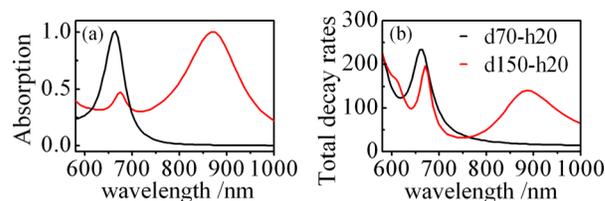


FIG. 1. (a) Normalized absorption spectra of cylinder d70-h20 (black) and d150-h20 (red). (b) Normalized total decay rates of a point dipole source near the cylinders.

For the cylinder d150-h20 for which the size becomes comparable to the incident light wavelength, the electric field can no longer be assumed uniform across the nanostructure. As a consequence of the retardation, quadrupolar mode is able to directly couple with the higher multipolar components of the incident wave.^{12,17} For comparison, the plasmon resonance modes of the cylinder are also calculated using a point source illumination; as expected the quadrupolar mode supported by the large cylinder is efficiently excited as shown in Fig. 1(b). It coincides with a previous paper that reported that the quadrupolar dark plasmon mode of a bipyramidal nanoparticle can induce a corresponding emission peak by a dipole source.¹⁸ All above calculations prove that the quadrupolar dark plasmon mode of a large size gold cylinder can become bright and can be excited by a dipole source or incident plane wave. Since bright modes couple to light, they also radiate, and this spectral feature can remarkably affect the two-photon emission process of the fluorophores near the nanostructures.

Now we investigate how the dipolar and quadrupolar resonance modes of the gold cylinders enhance TPEF simultaneously, which modify both excitation and emission rate of a single emitter. Here, the cylinder d150-h20 is studied in detail as its dipolar resonance lies at wavelength of 880 nm and quadrupolar resonance at wavelength of 670 nm. These wavelengths are placed in a region closed to (i) the emission of Cy5 molecules (fluorophore widely used in biochemistry, emission maximum 670 nm—absorption maximum at 650 nm for one-photon process)¹⁹ and (ii) the widely used two-photon fluorescence excitation source laser that lies in the near-infrared region (750–950 nm). For comparison, cylinder d70-h20 and d120-h20 are also calculated in detail, as they have only one clear dipolar resonance at 670 nm or 780 nm in wavelength, respectively. Fig. 2(b) shows the Purcell factor F for the three cylinders with the same distance between the emitter and the cylinder surface. Purcell factor (i.e., the radiative decay rates enhancement) of cylinder d150-h20 displays a double-peak behavior at 880 nm and 670 nm in wavelength, reflecting these two modes strongly radiating to the far field. Cylinder d70-h20 and d120-h20 have only one characteristic peak as expected. Given that the initial quantum efficiency η_0 is 0.3 at $\lambda = 670$ nm, we can calculate the relative fluorescence intensity of Cy5 (as shown in Table I) excited by light at wavelength of 880 nm for cylinder d70-h20 and d150-h20, and the excitation wavelength is 820 nm for cylinder d120-h20.

By comparing the two-photon fluorescence behaviors of the cylinders, it is clear that LSPRs overlapping with both the excitation and the emission band of the emitter

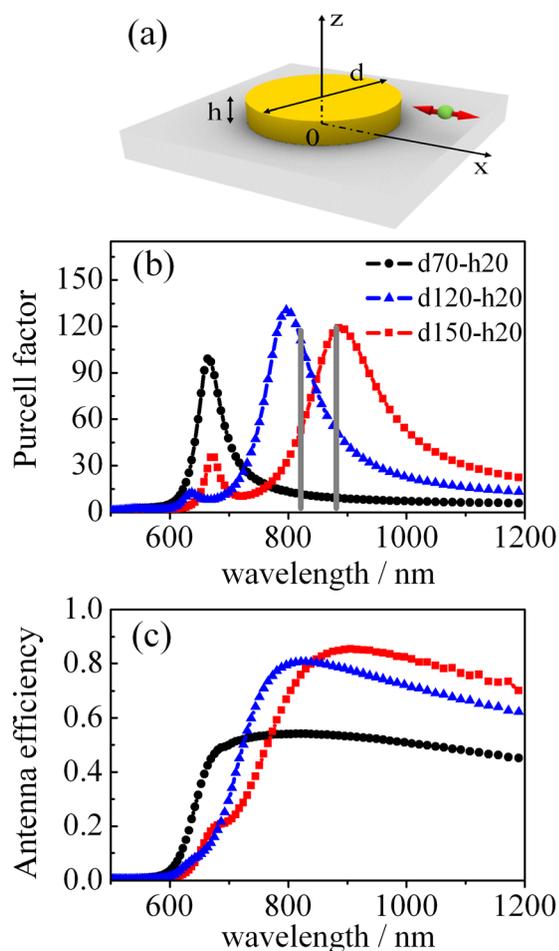


FIG. 2. (a) Configuration of single dipole emitter in the vicinity of a cylinder. The dipole is positioned at the same height with the cylinder, with the dipole-cylinder separation 8 nm. The emitting dipole orientated along x axis. Normalized Purcell factor F (b) and antenna efficiency η_a (c) for different cylinders (black circles for cylinder d70-h20, blue triangles for d120-h20 and red rectangles for d150-h20). The gray lines in (b) indicate the two-photon excitation wavelength (880 nm for cylinder d70-h20 and 150-h20, 820 nm for d120-h20).

would result in the highest fluorescence enhancement. The cylinder d70-h20 has a strong resonance at the Cy5 emission band, thus resulting in a high quantum efficiency as shown in Table I. This quantum efficiency is related to a large quantum efficiency corresponding to the high Purcell factor F and to the antenna efficiency η_a (Fig. 2(c)) given by Eq. (1). This can be well understood in the way that the Purcell factor F is large enough, which improves the quantum efficiency so that it can approach to the antenna efficiency η_a . Although cylinder d70-h20 provides the highest quantum efficiency, its

plasmon has no resonance within the near-infrared incident light, then very low excitation rate, and small field enhancement are obtained, resulting in the weakest fluorescence intensity enhancement. The nonlinear feature of two-photon excitation implies the quadratic dependence of absorption on the excitation light intensity, so it is essential to design plasmon resonances corresponding to excitation wavelength to achieve the strongest local field enhancement. As we can see in Table I, both cylinders d150-h20 and d120-h20 present obvious surface plasmon resonance modes in near-infrared region and result in high field enhancement strongly coupled to the excited light. For comparison, the local field at wavelength of 880 nm for the cylinder d150-h20 and at wavelength of 820 nm for d120-h20 is calculated to obtain almost the same enhancement effect, then, the difference in fluorescence performance originates from the deviation of quantum efficiency. As seen in Table I, the cylinder d150-h20 has the higher fluorescence enhancement than the d120-h20 one. Due to the presence of the quadrupolar plasmon resonance of the cylinder d150-h20, the antenna efficiency at around 670 nm is higher than that of the cylinder d120-h20, so the fluorescence intensity is higher. The quadrupolar resonance provide more efficient coupling between the molecular emissions and the radiative LSPR modes.

The advantages of quadrupolar plasmon resonance lying at the molecule fluorescence emission can be further demonstrated by the distance dependence of surface enhanced TPEF. The surface enhanced fluorescence effect is usually distance dependent, and the LSPR mode could significantly influence the distance behavior. Figure 3 demonstrates the excitation enhancement (square of the local field enhancement), quantum efficiency, and relative fluorescence intensity as a function of the separation between the emitter and the cylinder (in other words, an emitter polarized along the x direction is placed at the various positions indicated in Fig. 2(a)). The excitation rate increases greatly at the very vicinity of the cylinder which is related to the field distribution around the cylinder. Both cylinder d150-h20 and d120-h20 have similar excitation enhancement at different distances by excitation light at wavelengths of 880 or 820 nm, respectively. Their quantum yields decline with separation decreasing due to the strong nonradiative loss of the metal, while that of the cylinder d120-h20 reduces more rapidly as shown in Fig. 3(b). Because the cylinder d120-h20 has no resonances at the molecular emission band, this leads to a lower quantum efficiency correlated to fluorescence quenching at immediate proximity of the surface. Thanks to the quadrupolar resonance mode, a large two-photon fluorescence signal can still be observed for emitter-metal separation as small as

TABLE I. Cy5 two-photon fluorescence characteristics with different cylinder sizes.

Cylinder	Excitation enhancement ($ E/E_0 ^4$)	Antenna efficiency (670 nm) ^a	Quantum efficiency (670 nm)	Enhancement factor (670 nm) ^b
d70-h20	117/880 nm ^c	0.45	0.44	173
d120-h20	17391/820 nm	0.14	0.13	7690
d150-h20	17800/880 nm	0.18	0.18	10596

^aAntenna efficiency at Cy5 emission maximum position 670 nm.

^bTwo-photon fluorescence enhancement factor for emission wavelength at 670 nm, with free Cy5 initial quantum efficiency is 0.3 at 670 nm.

^cTwo-photon excitation rate enhancement under a certain excitation wavelength.

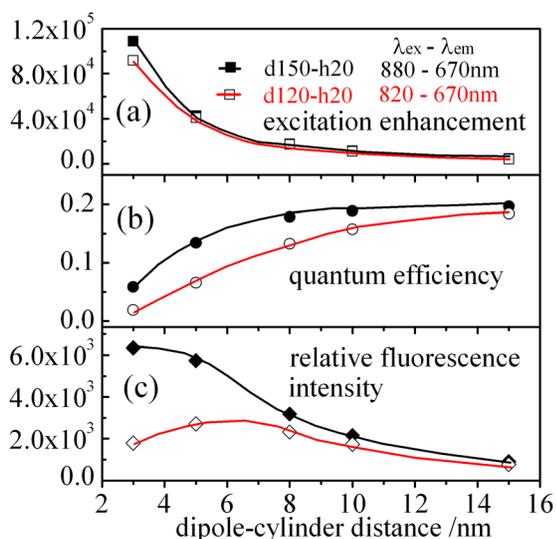


FIG. 3. Two-photon excitation rates enhancement (a), normalized quantum efficiency (b) and relative two-photon fluorescence intensity (c) for an emitter coupled to the cylinder d150-h20 and d120-h20 as a function of the emitter-cylinder separations. The emission at wavelength of 670 nm is the same for both cylinders, the excitation wavelengths are at 880 nm for the cylinder d150-h20 and at 820 nm for the cylinder d120-h20.

3 nm, which means that the quenching process is not yet dominating. In contrast, fluorescence for the molecules very closed to cylinder d120-h20 displays obvious quenching effects. Plasmon resonance overlapping with molecular emission band permits to effectively reduce the quenching effect. Such a property has been widely reported in theoretical and experimental studies for one-photon metal-enhanced fluorescence,⁹ and it is again confirmed and effective in metal-enhanced TPEF process.

In order to fully understand the metallic nanostructure enhanced TPEF, we investigate further how the dipole orientation and dipole-metal 3D configurations influence the fluorescence intensity. To be consistent with the experimental conditions, the cylinder is under illumination of light propagating along the z direction and polarized along the x direction. Several typical positions and dipole orientations are calculated and the results are shown in Fig. 4. The emitter-cylinder separation is fixed at 8 nm. As we can see the Purcell factors plotted in Fig. 4(c), the coupling strength between the emitter and cylinder presents anisotropic behavior for different configurations of molecule relative to the cylinder. For position A and B, the strong coupling is only effective for the dipole orientated along x axis. A dipole orientated along z axis even presents a negative coupling effect as the fluorescence intensity is suppressed than the situation for free molecule indicated in Fig. 4(d). At position C, Purcell factor for dipole orientated along z direction increases greatly, which could be due to the excitation of higher multipoles. In such a case, the incident light is z-polarized and propagating along the x axis. Because of the very weak local field, dipole at position C with orientation e_z displays no fluorescence enhancement. At position D, the coupling between the dipole and the cylinder remains still weak, leading to only little fluorescence enhancement. The above investigations also provide guidelines for TPEF experiments. For fluorophores in the vicinity of the cylinder surfaces, only those

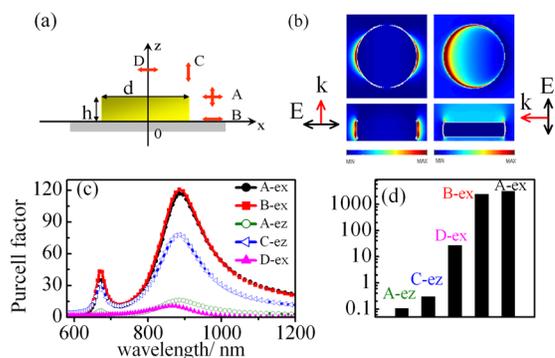


FIG. 4. Two-photon fluorescence dependences on different dipole-cylinder 3D configurations. (a) The configuration of the system. (b) Field distributions at x-y plane and x-z plane near the cylinder d150-h20. The excitation wavelength is at 880 nm, and the propagating and polarization directions are also indicated. Purcell factor (c) and relative TPEF intensity at emission wavelength of 670 nm (d) for different configuration situations.

conjugated to the side surfaces with proper orientation can achieve significant TPEF enhancement. Field distributions of the cylinder d150-h20 illuminated by 880 nm planar continuous wave polarized along x and z direction are also calculated and plotted in Fig. 4(b) for a better understanding of the orientation and configuration dependent phenomena. The optical field enhancement exhibits an asymmetric distribution at the vicinity of the cylinder, and the corresponding TPEF has a strong polarization dependence. Taking into account that the fluorescence enhancement depends not only on the local field but also on the quantum efficiency, the designed cylinder with dipolar and quadrupolar plasmon resonances displays the distinct advantages for enhancing two-photon fluorescence. Furthermore, we adjust the diameter d and height h of the cylinder structure to optimize the fluorescence enhancement. Several other cylinders with almost same dipolar and quadrupolar plasmon resonance peaks as the cylinder d150-h20 are selected and we find the Purcell factor and field enhancement are decreased as the dimensions of cylinder increase. Considering the feasibility of nanofabrication in experiments, we take the cylinder d150-h20 as the optimized structure to achieve most intense two-photon fluorescence (see supporting information).

Additionally, it should be noted that we mainly consider how the metallic nanostructures modify the excitation and emission rates during the metal-enhanced TPEF as the conventional way in the metal-enhanced one-photon excitation fluorescence.¹¹ The molecular excitation rates is only characterized by the local field enhancement factor; meanwhile, the emission probability represented by quantum efficiency is influenced for the reason that metallic nanostructures alter the radiative and nonradiative decay rates of the fluorophores. As a result, final fluorescence intensity approximately behaves as the product of these two processes. Nevertheless, we think that the process of the plasmonic nanostructure surface enhanced TPEF is more complex in practice. Our theoretical simulations do not include some probable factors during the interaction of between metallic nanostructures and nearby fluorophores. For instance, there are two possible extra energy transfer channels between the metallic nanostructures and the nearby fluorophores. First, plasmonic nanostructures absorbing the illuminated incident light

induce strong localized electric field on the surfaces and enable some nonlinear optical effects, like second harmonic generation²⁰ or four-wave mixing processes.²¹ Doubled frequency of the fundamental near-IR light or four-wave mixing frequency can be absorbed directly by the nearby fluorophores. Second, light-irradiated plasmonic nanostructures may also emit a two-photon luminescence.²² Then the photoluminescence light can overlap the fluorophore absorption band, thus also leading to the fluorescence excitation enhancement. In such cases, metallic nanostructures with nonlinear optical response or photoluminescence emission can serve as an extra source to excite emitters. In a recently reported metal-enhanced TPEF experiment, ordered gold cylinders array with plasmon resonance designed overlapping with the Cy5 linear absorption band was observed for a high TPEF enhancement.⁸ The above mentioned energy transfer effects may provide other explanations for metal-enhanced TPEF process, which are beyond the scope of this study.

In conclusion, we demonstrated the concept that the metallic nanostructure with multipolar plasmon resonance modes can be utilized to enhance two-photon fluorescence efficiently. Dipolar resonance of a gold nano-cylinder was tuned to couple to the incident light and induced large local field enhancement, and the quadrupolar mode can resonance with the emission of the fluorescent molecule to enhance the emission process. Engineering the optical properties of metallic nanostructures, excitation and emission processes of two-photon excited fluorescence could be highly enhanced simultaneously through a single nanostructure. We believe that this study offer an opportunity for metal-enhanced fluorescence and provide promises for two-photon fluorescence applications.

This work was supported by the National Basic Research Program of China (Grant Nos. 2009CB930504 and 2007CB307001) and the National Natural Science Foundation of China (Grant Nos. 61008026, 10821062, 90921008).

¹F. Helmchen and W. Denk, "Deep tissue two-photon microscopy," *Nat. Methods* **2**, 932 (2005)

²P. T. C. So, C. Y. Dong, B. R. Masters, and K. M. Berland, *Annu. Rev. Biomed. Eng.* **2**, 399 (2000)

³D. W. Piston, *Trends Cell Biol.* **9**, 66 (1999).

⁴M. Albota, D. Beljonne, J. L. Bredas, J. E. Ehrlich, J. Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCoord-Maughon, J. W. Perry, H. Rockel, M. Rmi, C. Subramaniam, W. W. Webb, X. L. Wu, and C. Xu, *Science* **281**, 1653 (1998).

⁵D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, and W. W. Webb, *Science* **300**, 1434 (2003).

⁶P. P. Pompa, L. Martiridonna, A. D. Torre, F. D. Sala, L. Manna, M. D. Vittorio, F. Calabi, R. Cingolani, and R. Rinaldi, *Nat. Nanotechnol.* **1**, 126 (2006); G. Lu, W. Li, T. Zhang, S. Yue, J. Liu, L. Hou, A. Li, and Q. Gong, *ACS Nano* **6**, 1438 (2012).

⁷X. Li, F.-J. Kao, C.-C. Chuang, and S. He, *Opt. Express* **18**, 11335 (2010); H. Kano and S. Kawata, *Opt. Lett.* **21**, 1848 (1996); C.-Y. Lin, K.-C. Chiu, C.-Y. Chang, S.-H. Chang, T.-F. Guo, and S.-J. Chen, *Opt. Express* **18**, 12807 (2010).

⁸J.-M. Jung, H.-W. Yoo, F. Stellacci, and H.-T. Jung, *Adv. Mater.* **22**, 2542 (2010).

⁹L. Rogobete, F. Kaminski, M. Agio, and V. Sandoghdar, *Opt. Lett.* **32**, 1632 (2007); F. Emmanuel and S. Gresillon, *J. Phys. D: Appl. Phys.* **41**, 013001 (2008); F. Tam, G. P. Goodrich, B. R. Johnson, and N. J. Halas, *Nano Lett.* **7**, 496 (2007); K. Munehika, Y. Chen, A. F. Tillack, A. P. Kulkarni, I. J.-L. Plante, A. M. Munro, and D. S. Ginger, *Nano Lett.* **10**, 2598 (2010); G. Lu, T. Zhang, W. Li, L. Hou, J. Liu, and Q. Gong, *J. Phys. Chem. C* **115**, 15822 (2011).

¹⁰J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Springer, New York, 2006), pp. 841–870.

¹¹C. Sonnichsen, T. Franzl, T. Wilk, G. von Plessen, and J. Feldmann, *Phys. Rev. Lett.* **88**, 077402 (2002); T. Hartling, P. Reichenbach, and L. M. Eng, *Opt. Express* **15**, 12806 (2007); T. Zhang, G. Lu, W. Li, J. Liu, L. Hou, P. Perriat, M. Martini, O. Tillement, and Q. Gong, *J. Phys. Chem. C* **116**, 8804 (2012).

¹²F. Hao, E. M. Larsson, T. A. Ali, D. S. Sutherland, and P. Nordlander, *Chem. Phys. Lett.* **458**, 262 (2008).

¹³H. Wang, Y. Wu, B. Lassiter, C. L. Nehl, J. H. Hafner, P. Nordlander, and N. J. Halas, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 10856 (2006); F. Hao, P. Nordlander, Y. Sonnefraud, P. V. Dorpe, and S. A. Maier, *ACS Nano* **3**, 643 (2009).

¹⁴Z. Yang, Z. Zhang, L. Zhang, Q. Li, Z. Hao, and Q. Wang, *Opt. Lett.* **36**, 1542 (2011); S. Zhang, K. Bao, N. J. Halas, H. Xu, and P. Nordlander, *Nano Lett.* **11**, 1657 (2011).

¹⁵A. Taflove and S. C. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method*, 3rd ed. (Artech House, Norwood, MA, 2005); F. Kaminski, V. Sandoghdar, and M. Agio, *J. Comput. Theor. Nanosci.* **4**, 635 (2007).

¹⁶P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**, 4370 (1972).

¹⁷J. P. Kottmann and O. J. F. Martin, *Opt. Lett.* **26**, 1096 (2001); K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B* **107**, 668 (2003).

¹⁸M. Liu, T.-W. Lee, S. K. Grey, P. Guyot-Sionnest, and M. Pelton, *Phys. Rev. Lett.* **102**, 107401 (2009).

¹⁹J. Lukomska, I. Gryczynski, J. Malicka, S. Makowicz, J. R. Lakowicz, and J. Gryczynski, *Biochem. Biophys. Res. Commun.* **328**, 78 (2005).

²⁰Y. Zhang, N. K. Grady, C. Ayala-Orozco, and N. J. Halas, *Nano Lett.* **11**, 5519 (2011).

²¹S. Palomba and L. Novotny, *Nano Lett.* **9**, 3801 (2009).

²²K. Imura and H. Okamoto, *J. Phys. Chem. C* **113**, 11756 (2009).

²³See supplementary material at <http://dx.doi.org/10.1063/1.4742148> for dipolar resonances for different cylinders diameters and height, and Purcell factor for different cylinders, with the same plasmon resonances peak positions.