Enormous enhancement of electric field in active gold nanoshells*

Jiang Shu-Min(蒋书敏)[a], Wu Da-Jian(吴大建)[a]†, Wu Xue-Wei(吴雪炜)[b], and Liu Xiao-Jun(刘晓峻)[b]‡

[a] *Faculty of Science, Jiangsu University, Zhenjiang* 212013, *China*
[b] *School of Physics, Nanjing University, Nanjing* 210093, *China*

(Received 9 September 2013; revised manuscript received 10 October 2013; published online 20 February 2014)

The electric field enhancement properties of an active gold nanoshell with gain material inside have been investigated by using Mie theory. As the gain coefficient of the inner core increases to a critical value, a super-resonance appears in the active gold nanoshell, and enormous enhancements of the electric fields can be found near the surface of the particle. With increasing shell thickness, the critical value of the gain coefficient for the super-resonance of the active gold nanoshell first decreases and then increases, and the corresponding surface enhanced Raman scattering (SERS) enhancement factor (*G* factor) also first increases and then decreases. The optimized active gold nanoshell can be obtained with an extremely high SERS *G* factor of the order of 10^{19}–10^{20}. Such an optimized active gold nanoshell possesses a high-efficiency SERS effect and may be useful for single-molecule detection.

Keywords: gold nanoshell, enhancement of electric field, surface-enhanced Raman scattering, gain material

PACS: 78.67.–n, 78.67.Bf, 36.40.Vz, 73.22.Lp **DOI:** 10.1088/1674-1056/23/4/047807

1. Introduction

Surface-enhanced Raman scattering (SERS) is one of the most powerful probing methods — non-destructive, real time, and enabling highly sensitive characterization — and it has been widely used in chemical sensing, medical diagnostics, bioanalysis, and environmental science.[1–6] SERS relies on the large localized electric fields that appear near nanoscale metal surfaces in response to optical excitation of their surface plasmons (SPs).[1] Many devices have been explored to enhance this effect.[7–14] For example, "hot spots" in metal nanoparticle aggregates can lead to an SERS enhancement factor (*G* factor) of about 10^{14}–10^{15}, which is enough for single-molecule detection.[7] In metal nanoparticle dimers, the *G* factor can reach about 10^{11}–10^{12} when the molecules are trapped at the hotspots between two particles.[8] However, the hotspot region in the whole nanosystem is very small, and hence the SERS effect is low in efficiency. In addition, some attempts are focused on metal nanoparticles with sharp corners,[9,10] which can cause strong electric field enhancements at the sharp corners or tips. Such a strong electric field can greatly enhance the SERS signal. However, it is not enough for single-molecule detection.

Bergman and Stockman[15] first proposed the phenomenon called surface plasmon amplification by stimulated emission of radiation (spaser) in a plasmonic nanostructure incorporating gain media. The metal nanoparticle incorporating gain media can be called the "active nanoparticle". The gain materials doped in the dielectric near the metal surface can couple with the plasmonic structure. Then the gain materials transfer energy to compensate the loss of SP and finally amplify the desired SP response. Spaser has been demonstrated experimentally with several active plasmonic designs and attracted extensive interest due to spaser particles' potential applications in optical metamaterials and ultrasmall lasers.[16–19] Noginov *et al.*[17] experimentally demonstrated a spaser-based nanolaser with a gold core and a dye-doped silica shell. Xiao *et al.*[18] reported that the incorporation of gain material in the high-local-field areas of a metamaterial makes it possible to fabricate an extremely low-loss and active optical NIM. Meng *et al.*[19] proposed a semi-shell-capped spaser with well-defined and unidirectional stimulated emission and highly effective laser output. On the other hand, Li *et al.*[20] introduced gain media into the core of cubic gold nanoboxes and obtained an extremely high SERS *G* factor of the order of 10^{16}–10^{17}. Such a large *G* factor relies on the combined contributions of the spaser and the sharp corners of the gold nanoboxes.

In this paper, we investigate the electric field enhancements of the gold nanoshell with gain-doped dielectric core by using Mie theory. A gold nanoshell is a simple and classic nanoparticle with advantages including tunable optical response, long-term stability, easy fabrication, and biocompatibility. When the gain coefficient of the inner core increases to a critical value, a super-resonance is found in the active gold nanoshell and an enormous enhancement of the electric fields

*Project supported by the National Basic Research Program of China (Grant No. 2012CB921504), the National Natural Science Foundation of China (Grant Nos. 51306072, 11174113, and 11204129), the Qing Lan Project of Jiangsu Province, China, and the Senior Talent Foundation of Jiangsu University (Grant No. 12JDG060).

†Corresponding author. E-mail: wudajian@ujs.edu.cn
‡Corresponding author. E-mail: liuxiaojun@nju.edu.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

is also observed. Such an enormous near field is sufficient for the single-molecule detection, which has not been given enough attention in the previous report.[16] Further design optimization for active gold nanoshells has been carried out, predicting that an extremely high SERS G factor of the order of 10^{19}–10^{20} can be realized.

2. Gold nanoshell with gain media

The geometry of the active gold nanoshell is shown in Fig. 1. The active gold nanoshell consists of a SiO_2 core with gain media surrounded by a thin gold shell. The radii of the inner core and outer shell are r_1 and r_2, respectively.

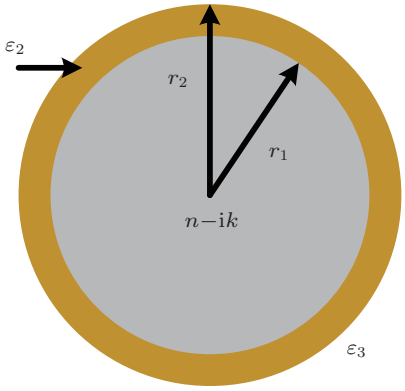


Fig. 1. (color online) Geometry of the active gold nanoshell.

The permittivity of the gold shell ε_2 has real and imaginary frequency-dependent components and should be affected by the scattering of the conduction electrons in particle surfaces. Therefore, ε_2 is usually described by replacing the ideal Drude part in the dielectric function with a size-dependent one, and can be expressed as[21]

$$\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} + \chi_\infty, \tag{1}$$

where the background susceptibility χ_∞ arises from the electron polarizability and interband transition, and ω_p is the bulk plasma frequency. Since the gold shell is thinner than the bulk electron mean free path of gold, the contribution of size-dependent electron scattering to the dielectric function becomes important. Thus the bulk collision frequency for gold can be modified as[21]

$$\gamma = \gamma_f + A\frac{V_f}{a}, \tag{2}$$

where γ_f is the bulk collision frequency and V_f is the Fermi velocity. We use $(r_2 - r_1)$ as the reduced electron mean free path a. For simple Drude theory and isotropic scattering, $A = 1$. The gain materials such as dye molecules,[17] quantum dots,[22] rare-earth ions,[16] and semiconductors[23,24] can be chosen to amplify the SP via stimulated emission under optical pumping. For simplicity, a complex refractive index for the inner core is set as $n - ik$. n is fixed at 1.43 for the host medium of SiO_2 and the gain coefficient k is related to the amount of optical gain induced by external pumping.[20] The surrounding medium is assumed to be air with $\varepsilon_3 = 1$. The scattering spectra, absorption spectra, and electric field enhancements of the active gold nanoshells can be calculated by using Mie scattering theory. The electromagnetic waves are expanded to spherical partial waves using vector spherical harmonics, and then Maxwell's boundary conditions are applied to resolve the unknown expansion coefficients of the scattered and interior waves. The scattering and absorption spectra of the nanoshells are expressed by the scattering efficiency Q_{sca} and absorption efficiency Q_{abs}, which can be obtained in Ref. [25]. To a good approximation, the SERS G factor can be expressed by the fourth power of the ratio of the total electric field $\boldsymbol{E}_{loc}$ at the molecule location to the incident excitation field $\boldsymbol{E}_{in}$[26,27]

$$G = |\boldsymbol{E}_{loc}/\boldsymbol{E}_{in}|^4, \tag{3}$$

where $\boldsymbol{E}_{loc} = \boldsymbol{E}_{sca} + \boldsymbol{E}_{in}$, and $\boldsymbol{E}_{sca}$ means the scattered field.

3. Results and discussion

Figure 2(a) shows the scattering and absorption spectra of the passive gold nanoshell ($k = 0$). Here, the radii of the inner core and outer shell r_1 and r_2 are fixed at 40 nm and 50 nm, respectively. A strong peak appears at about 639.5 nm, which is due to the dipole resonances in the gold nanoshell. We also note that a weak peak appears at about 457 nm, which arises from the interband transitions in the Au state. $Q_{abs} > Q_{sca}$ indicates that the absorption in this gold nanoshell is dominant. When the k-value increases a little, the profiles of the scattering and absorption spectra of the active gold nanoshell are similar to those of the passive gold nanoshell. Meanwhile, there are small increases in Q_{sca} and Q_{abs}, and the line widths of the scattering and absorption peaks are reduced. As the k-value increases to 0.2889, the absorption at a resonance wavelength of 639.5 nm becomes zero and the corresponding Q_{sca} increases to about 25.8, as shown in Fig. 2(b). In this case, the optical losses at the resonance wavelength are compensated by the gain media. In addition, a distinct peak appears at about 554 nm, which is due to the quadrupole resonance in the nanoshell. The quadrupole plasmon peak in the active gold nanoshell is also compensated by the gain media and hence the increased peak intensity. When the k-value increases to a critical value at 0.4188, a super SP resonance appears in the active gold nanoshell at about 629.5 nm, as shown in Fig. 2(c). The peak intensity of Q_{sca} reaches about 1.91×10^7, which is about 8.16×10^6 times that for $k = 0$. We also find that the Q_{abs} shows a great negative enhancement. The negative Q_{abs}-value means that the scattered radiation is amplified by the energy transferred from the gain media.[16] Compared to the

passive gold nanoshell, the wavelength of the super-resonance of active gold nanoshells shows a blue shift from ∼639.5 nm to ∼ 629.5 nm. The blue shift indicates that the gain media may influence the plasmon resonance energy of the active gold nanoshell. The energy transition from the gain media increases the oscillation strength of the free electrons and hence the increased resonance energy. When the k-value continues to increase, the super-resonance breaks down, leading to decreased values of $Q_{\rm sca}$ and $Q_{\rm abs}$ and increased line-widths, as shown in Fig. 2(d).

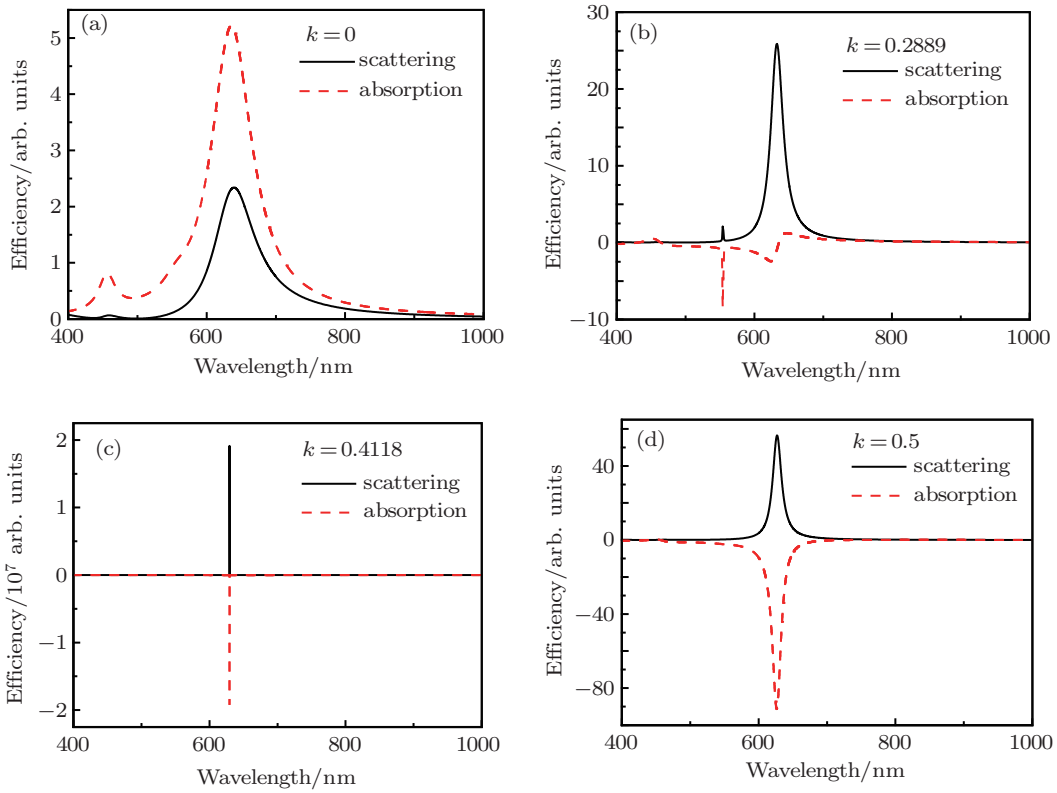


Fig. 2. (color online) Scattering and absorption spectra of the active gold nanoshells with (a) $k = 0$, (b) $k = 0.2889$, (c) $k = 0.4118$, and (d) $k = 0.5$. Here r_1 and r_2 are 40 nm and 50 nm, respectively.

Figure 3(a) shows the contour plot of the $|\boldsymbol{E}_{\rm loc}/\boldsymbol{E}_{\rm in}|^4$ in the passive gold nanoshell at dipole resonance wavelength of 639.5 nm. Here, r_1 and r_2 are fixed at 40 nm and 50 nm, respectively. The larger enhancements of the electrical fields occur along the incident polarization and are located only within a few nanometers of the outer shell surface, which can be well interpreted by the dipole plasmon resonance.[9] The maximal G-value is about 5500. The larger field enhancements in the shell occur perpendicular to the incident polarization (not along the incident polarization). According to plasmon hybridization theory,[28] the lower-energy resonance corresponds to a symmetric coupling between a gold sphere and a gold cavity, which results in the same sign of charges on both the inner and outer surfaces of the nanoshell along the incident polarization. Thus, the field lines inside the shell repel each other in the poles along the incident polarization and bunch up at the poles perpendicular to the polarization direction. Figure 3(b) shows the enhancement distribution of the electric fields in the active gold nanoshell at super-resonance. The wavelength is 629.5 nm and the k-value is 0.4118. In this case, the distribution of the electric fields in the active gold nanoshell is similar to that observed in the passive gold nanoshell. However, an enormous enhancement of the electric fields is found in the active gold nanoshell, which was not realized in the previous report.[16] The maximal G-value can reach about 3.25×10^{17}, which is about 5.92×10^{13} times that of the passive gold nanoshell.

Figure 4(a) shows the variation of the G factor in the passive gold nanoshell along the y axis at the resonance wavelength. The enhanced electric fields outside the shell decrease very quickly, and the larger electric fields are located only within 2 nm–3 nm of the outer shell. In Fig. 4(b), at the super-resonance of the active gold nanoshell, the G-value decreases from about 3.25×10^{17} on the shell surface to about 3.95×10^{15} at a location of 15 nm away from the shell surface. Thus, the hotspot scale in the active gold nanoshell is also greatly enhanced. Meanwhile, the electric fields in the inner core are also enhanced and the G factor can reach $\sim 10^{16}$.

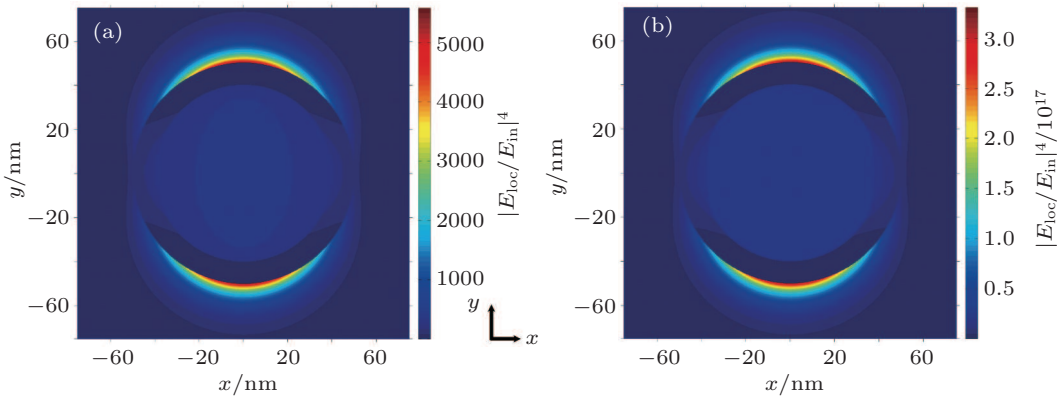


Fig. 3. (color online) Contour plots of $|\boldsymbol{E}_{loc}/\boldsymbol{E}_{in}|^4$ in (a) the passive gold nanoshell at dipole resonance wavelength of 639.5 nm and (b) the active gold nanoshell at super-resonance of 629.5 nm ($k = 0.4118$). Here, r_1 and r_2 are fixed at 40 nm and 50 nm, respectively.

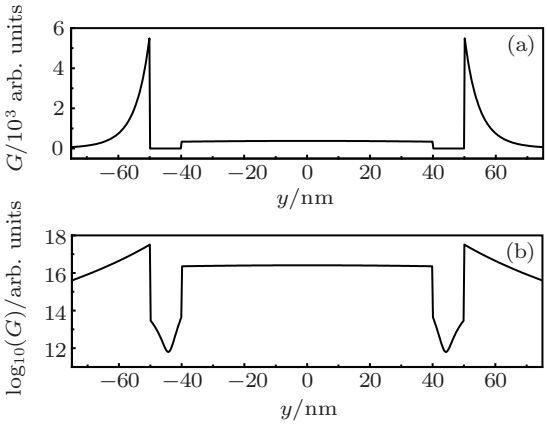


Fig. 4. Variations of the G factor along the y axis in (a) the passive gold nanoshell at the dipole resonance and (b) the active gold nanoshell at the super-resonance. Here r_1 and r_2 are fixed at 40 nm and 50 nm, respectively.

We further investigate the influence of the shell thickness on the electric field enhancements in the active gold nanoshells. In Fig. 5(a), the dash–circle line for the left-hand scale represents the variation of the super-resonance wavelength of the active gold nanoshell as a function of shell thickness, while the dash–square line for the right-hand scale shows the variation of the corresponding gain coefficient for the super-resonance. Here, the radius of the inner core is fixed at 40 nm. With increasing thickness of the gold shell, the wavelength of the super-resonance in the active gold nanoshell shows a blue shift. At the same time, the gain coefficient for super-resonance first decreases from 0.745 at $r_2 - r_1 = 2$ nm to 0.3893 at $r_2 - r_1 = 8$ nm, and then increases to 0.548 at $r_2 - r_1 = 15$ nm. Note especially that with increasing shell thickness, the maximal G-value obtained in the active gold nanoshells first increases from 7.15×10^{17} at $r_2 - r_1 = 2$ nm to 7.62×10^{19} at $r_2 - r_1 = 8$ nm and then decreases to 7.67×10^{15} at $r_2 - r_1 = 15$ nm, as shown in Fig. 5(b). The plasmon resonances in the gold nanoshell can be explained as the coupling between a sphere mode on the outer surface and a cavity mode on the inner surface of the shell.[28] When the shell thickness is very thin, the coupling between the two modes is very strong and leads to high metallic losses. Under this condition, the larger gain threshold is due to the higher metallic losses. The increased thickness of the gold shell leads to a decrease of the critical value of the gain coefficient. On the other hand, the increased thickness of the gold shell also increases the gold component, hence, the increased metallic losses. The competition between the two mechanisms causes the minimum of the gain coefficient at $r_2 - r_1 = 8$ nm.

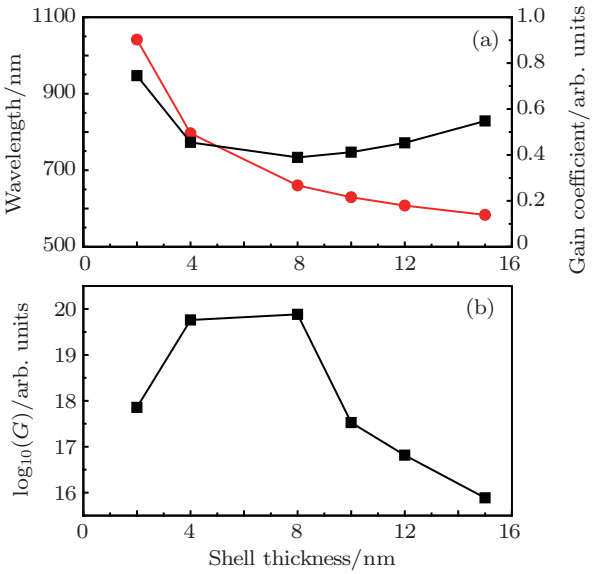


Fig. 5. (color online) (a) Dependencies of the super-resonance wavelength (dash–circle line for the left-hand scale) and the critical value of k (dash–square line for the right-hand scale) for the active gold nanoshell on the thickness of the gold shell. (b) Variation of the corresponding G factor. Here r_1 is fixed at 40 nm.

The solid line in Fig. 6(a) shows the log plot (base 10) of the maximal G factor in the active gold nanoshell as a function of the k-value. Here, r_1 and r_2 are fixed at 40 nm and 48 nm, respectively. The calculated wavelength of 660.3 nm is the wavelength of the super-resonance. The dashed line represents the maximal G factor in the passive gold nanoshell. With

the k-value increasing, the SERS G factor first increases and then decreases. The maximum of the G factor (7.62×10^{19}) is found at the critical value of $k = 0.3893$. When $k < 0.87$, the G factors in the active nanoshell are larger than that obtained in the passive gold nanoshell. When $k > 0.87$, the effect of the gain media on the near-field enhancements in the active gold nanoshell is regressive. Figure 6(b) shows the dependence of the G factor at the super-resonance of the active gold nanoshell on the d-value. Here, d indicates the distance away from the outer surface of the nanoshell. With the d-value increasing, the G factor decreases from 7.62×10^{19} at $d = 0$ nm to 3.48×10^{16} at $d = 50$ nm. The large hotspot region means that this optimized active gold nanoshell possesses high SERS efficiency.

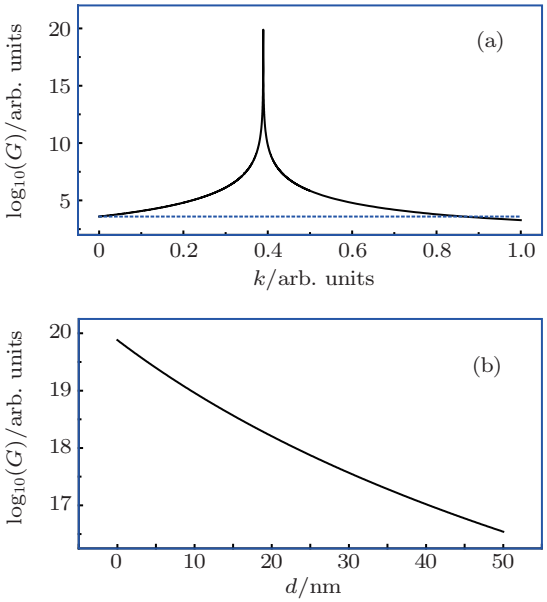


Fig. 6. (color online) (a) The log plot (base 10) of the maximal G factor in the active gold nanoshell as a function of the k-value. (b) Dependence of the G factor at the super-resonance on the d-value. Here, r_1 and r_2 are fixed at 40 nm and 48 nm, respectively; d is the distance away from the outer surface of the nanoshell.

4. Conclusions

The electric field enhancement properties of the active gold nanoshell have been investigated by using Mie theory. As the gain coefficient increases to a critical value, a super-resonance has been found in the active gold nanoshell, and this super-resonance induces the enormous enhancement of the electric fields. With the thickness of the outer gold shell increasing, the critical value of the gain coefficient for the super-resonance first decreases and then increases while the corresponding SERS G factor first increases and then decreases. An extremely high SERS G factor on 10^{19}–10^{20} can be obtained in the optimized active gold nanoshell. It is further found that a high SERS G factor of about 10^{16} can be obtained at a location of 50 nm away from the surface of the nanoshell. Thus, the optimized active gold nanoshell has a high-efficiency SERS effect and would serve well for single-molecule detection.

References

[1] Schatz G C 1984 *Acc. Chem. Res.* **17** 370
[2] Su Q Q, Ma X Y, Dong J A, Jiang C Y and Qian W P 2011 *ACS Appl. Mater. Interfaces* **3** 1873
[3] Schuetz M, Mueller C I, Salehi M, Lambert C and Schluecker S 2011 *J. Biophoton.* **4** 453
[4] Chen L, Han X X, Yang J X, Zhou J, Song W, Zhao B, Xu W Q and Ozaki Y 2011 *J. Colloid Interface Sci.* **360** 482
[5] Gopalakrishnan A, Malerba M, Tuccio S, Panaro S, Miele E, Chirumamilla M, Santoriello S, Dorigoni C, Giugni A, Zaccaria R P, Liberale C, De Angelis F, Razzari L, Krahne R, Toma A, Das G and Fabrizio Di E 2012 *Ann. Phys.* (Berlin) **524** 620
[6] Wang J, Huang L Q, Tong H M, Zhai L P, Yuan L, Zhao L H, Zhang W W, Shan D Z, Hao A W and Feng X H 2013 *Chin. Phys. B* **22** 047301
[7] Nie S and Emory S R 1997 *Science* **275** 1102
[8] Schuck P J, Fromm D P, Sundaramurthy A, Kino G S and Moerner W E 2005 *Phys. Rev. Lett.* **94** 017402
[9] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 *J. Phys. Chem. B* **107** 668
[10] Esenturk E N and Walker A R H 2008 *J. Raman Spectr.* **40** 86
[11] Cong C, Wu D J and Liu X J 2012 *Acta Phys. Sin.* **61** 037301 (in Chinese)
[12] Wu D J, Jiang S M, Cheng Y and Liu X J 2012 *Gold Bull.* **45** 197
[13] Deng C Y, Zhang G L, Zou B, Shi H L, Liang Y J, Li Y C, Fu J X and Wang W Z 2013 *Chin. Phys. B* **22** 106102
[14] Ahn H J, Thiyagarajan P, Jia L, Kim S I, Yoon J C, Thomas E L and Jang J H 2013 *Nanoscale* **5** 1836
[15] Bergman D J and Stockman M I 2003 *Phys. Rev. Lett.* **90** 027402
[16] Gordon J A and Ziolkowski R W 2007 *Opt. Express* **15** 2622
[17] Noginov M A, Zhu G, Belgrave A M, Bakker R, Shalaev V M, Narimanov E E, Stout S, Herz E, Suteewong T and Wiesner U 2009 *Nature* **460** 1110
[18] Xiao S M, Drachev V P, Kildishev A V, Ni X J, Chettiar U K, Yuan H K and Shalaev V M 2010 *Nature* **466** 735
[19] Meng X G, Guler U, Kildishev A V, Fujita K, Tanaka K and Shalaev V M 2013 *Sci. Rep.* **3** 1241
[20] Li Z Y and Xia Y N 2010 *Nano Lett.* **10** 243
[21] Averitt R D, Westcott S L and Halas N J 1999 *J. Opt. Soc. Am. B* **16** 1824
[22] Klimov V I, Ivanov S A, Nanda J, Achermann M, Bezel I, McGuire J A and Piryatinski A 2007 *Nature* **447** 441
[23] Ma R M, Oulton R F, Sorger V J, Bartal G and Zhang X 2010 *Nature Mater.* **10** 110
[24] Flynn R A, Kim C S, Vurgaftman I, Kim M, Meyer J R, Mäkinen A J, Bussmann K, Cheng L, Choa F S and Long J P 2011 *Opt. Express* **19** 8954
[25] Bohren C F and Huffman D R 1983 *Absorption and Scattering of Light by Small Particles* (New York: Wiley)
[26] Kneipp K, Wang Y, Kneipp H, Perelman L T, Itzkan I, Dasari R R and Feld M S 1997 *Phys. Rev. Lett.* **78** 1667
[27] Zhao K, Xu H X, Gu B H and Zhang Z Y 2006 *J. Chem. Phys.* **125** 081102
[28] Prodan E, Radloof C, Halas N J and Nordlander P 2003 *Science* **302** 419