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Theoretical investigation on near-infrared and visible absorption spectra of nanometallic aluminium with oxide coating in nanoenergetic materials: size and shape effects*

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The effects of metal core dimension, oxide shell thickness and ellipsoid aspect ratio of Al–Al_2O_3 core-shell nanoparticles on the near-infrared and visible absorption spectra of nanocomposite Al–Al_2O_3/nitrocellulose(NC) film are investigated by numerical calculations. Both the size-dependent interband transitions and frequency-dependent free electron damping of the nanometallic aluminium are taken into account in the calculations. Oxidation effect of nanoaluminium is also analysed. It is shown that oxidation may enhance but may also reduce the optical absorption, depending on the excited light energy and initial dimension of nanoparticle. Metal core size and excited light energy dominate the absorption characteristic. The absorption ability of ellipsoidal nanoparticles is larger than that of spheroidal nanoparticles and increases by the square index as the aspect ratio increases. These calculations will provide some significant theoretical guidance for the preparation and laser ignition of nanoenergetic materials.

Keywords: core-shell nanoparticle, optical absorption, interband transition, nanoenergetic material
PACC: 7865, 7830E, 7820D

1. Introduction

Nanoenergetic materials have attracted much attention because of their wide applications in defense and military fields.[1,2] It is known that nanometallic aluminium additives to energetic formulations can improve performance due to the high combustion enthalpies.[3−5] Laser ignition of nanoenergetic materials is a novel ignition technology in aviation field due to the advantages of security and reliability.[6] Knowledge of the optical absorption properties of nanometallic particles will redound to an understanding of the ignition energy and time, thereby allowing materials to be tailored for specific applications.[7]

The size and the shape of nanoparticles are crucial parameters that determine their absorption characteristics.[8−12] Recently, most researches about the size and the shape effects of nanoparticles have been performed for the noble metals which are used in chemical and biological sensors[10,13] or some optical apparatus.[14−17] However, few experimental reports are involved with the nanometallic aluminium as the additives of nanoenergetic materials.[18] Yang *et al*[18] measured the absorption coefficient of Al–Al_2O_3 nanoparticles embedded in an NC film and found the absorption intensity was size-dependent. But they did not give any quantitative relationship. Wang *et al*[19] indicated that the Al_2O_3 layer in Al–Al_2O_3/NC nanoenergetic materials played an important and non-negligible role in laser ignition. However, they were concerned more about the dynamic effect of Al_2O_3 layer but did not examine its effect on the optical absorption. Very early, Ruppin[20] and Simanek[21] theoretically studied the far-infrared absorption of Al–Al_2O_3 core-shell nanoparticle and showed oxide layer dominated the optical absorption of nanoparticle. However in a near-infrared region, the Al_2O_3 almost is transparent and has no reflection and absorption to light.[22] Furthermore, the size-dependent interband transitions of aluminium are prominent in this region. Therefore it is necessary to study the near-infrared and visible absorption properties of Al–Al_2O_3

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nanoparticle further.

In practice, the ellipsoidal shape nanoparticles cannot be excluded during the process of preparation of spheroidal nanoparticles due to the difficulty in controlling complex environments.[23] Also, some nanometallic particles, such as aluminium particles, are easily oxidized.[18,19] The variations in shape and size are responsible for the absorption characteristics. In this paper, we theoretically investigate the effects of shape and dimension on the optical absorption of Al–Al_2O_3 nanoparticles embedded in a transparent NC matrix in a near-infrared and visible region by Mie theory together with the known additional contribution of dielectric function from interband transitions for aluminium. These results could be find their applications in laser ignition of nanoenergetic materials.

2. Theory

Mie theory[24−26] has been widely used in describing the absorption spectra of spheroidal nanoparticles. The important and complicated parameter in Mie theory is the dielectric function of metal. Metallic dielectric function comes generally from two parts of contributions: free electron intraband transitions and electronic interband transitions.

2.1. Metallic dielectric function

The contributions of both the free electron intraband transition and the electronic interband transitions to the dielectric function of nanometallic aluminium should be considered for the near-infrared and visible optical absorptions.[22,27] The free-electron dielectric function $\varepsilon_{\rm d}\ (\omega)$ is described by the Drude theory as[27,28]

$$\varepsilon_{\rm d}(\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2 + {\rm i}\gamma\omega}, \tag{1}$$

where $\omega_{\rm p}$ is the plasmon frequency and expressed as $\omega_{\rm p} = n_{\rm e}e^2/m\varepsilon_0$, with $n_{\rm e}$, e, m, and ε_0 being the number density of conduction electrons, the electron charge, the electronic effective mass, and the permittivity of free space, respectively; ω is the optical angular frequency; γ is the free-electron damping coefficient which is size-dependent and may be written as $\gamma = a + b\omega + c\omega^2$, with a, b and c being the parameters.[29] The interband-transition dielectric function obeys the Lorentz oscillator model.[27,30] Taneja and Ayyub[29] considered the interband transitions at a single resonance frequency and the continuous interband transitions were modeled by integrating Lorentz oscillator model in order to explain the colour change of Ag nanoparticles. The interband-transition dielectric function $\varepsilon_{\rm I}(\omega)$ is expressed as

$$\varepsilon_{\rm I}(\omega) = \rho\omega_{\rm p1}^2 \int_{\omega_1}^{\omega_2} \frac{1}{\omega_1^2 - \omega^2 - {\rm i}\gamma_1\omega}{\rm d}\omega_1, \tag{2}$$

where ρ is the number density of interband-transition frequency, $\omega_{\rm p1}$ is the interband-transition plasma resonance frequency, γ_1 is the interband-transition damping coefficient, ω_1 is the interband-transition onset frequency, and ω_2 is the interband-transition upper bound frequency. Then the metallic dielectric function $\varepsilon(\omega)$ is the sum of $\varepsilon_{\rm d}\ (\omega)$ and $\varepsilon_{\rm I}(\omega)$

$$\varepsilon(\omega) = \varepsilon_{\rm d}(\omega) + \varepsilon_{\rm I}(\omega). \tag{3}$$

2.2. Optical absorption of core-shell nanoparticle

Mie theory is a simple and exact solution to Maxwell's equations relevant to the nanoparticles to describe the absorption spectra of spherical particles.[31] Aden and Kerker[32] and Moskovits *et al*[24] extended Mie theory to core-shell particles, thereby allowing one to calculate absorption spectra. In quasi-static approximation the universal polarizability formula for spheroidal and ellipsoidal core-shell nanoparticles is[27]

$$\alpha_j = \frac{4}{3}\pi c_1c_2c_3 \frac{\{(\varepsilon_2 - \varepsilon_{\rm m})[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(L_j^{(1)} - gL_j^{(2)})] + g\varepsilon_2(\varepsilon_1 - \varepsilon_2)\}}{\{[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(L_j^{(1)} - gL_j^{(2)})][\varepsilon_{\rm m} + (\varepsilon_2 - \varepsilon_{\rm m})L_j^{(2)}] + gL_j^{(2)}\varepsilon_2(\varepsilon_1 - \varepsilon_2)\}}, \tag{4}$$

where ε_1, ε_2 and $\varepsilon_{\rm m}$ are the dielectric functions of the core, the shell and the embedding medium, respectively; $g = a_1a_2a_3/(c_1c_2c_3)$ is the volume fraction of the core occupying the core-shell nanoparticle, with a_1, a_2, a_3 and c_1, c_2, c_3 being the semi-axis lengths in Descartes coordinate orientations of core and core-

shell nanoparticle, respectively; L_j (j=1, 2, 3) represent the shape depolarization factors in three coordinate orientations; superscripts (1) and (2) represent the core and the core-shell nanoparticle, respectively. An important parameter for describing the optical absorption property is the mass absorption coefficient, which is the absorption coefficient per unit mass density. For our composite film, the mass absorption coefficient can be expressed as

$$A = n\frac{2\pi\varepsilon_{\mathrm{m}}^{\frac{1}{2}}}{\lambda m_{\mathrm{Al}}}V_{\mathrm{sam}}\mathrm{Im}\left(\sum_{j=1}^{3}\alpha_j\right), \tag{5}$$

where m_{Al} is the Al mass, V_{sam} is the volume of thin film sample, and n is the number density of nanoparticle.

2.3. Size dependence of dielectric function

Usually, the size dependence of dielectric function is assumed to be determined by the contribution of free electron. Here, our calculations are involved with size dependence of interband-transition onset frequency ω_1, which stems from the small size effect and surface effect of nanoparticle. The two effects cause the decrease of atoms density of surface and the surface atom coordination imperfection, which lead to the contraction of lattice and thus the increase of inner stress of nanoparticle.[33,34] With nanoparticle size reducing, inner stress increases according to the relation p=$2\gamma_{\mathrm{s}}/r$, where γ_{s} is the nanoparticle surface strain and r is the radius of nanoparticle.[35] Increased inner stress largens the superposition of electronic wave function and narrows the energy gap. So the interband-transition onset frequency proportional to the energy gap decreases. We indicate that the interband-transition onset frequency diminishes linearly as the nanometallic aluminium diameter d decreases from 30 to 120 nm by simulating the absorption spectra. The linear relationship is

$$\hbar\omega_1 = 1.75 + 0.003d, \tag{6}$$

where the unit of d is nanometer. The detail descriptions have been given in our previous papers (unpublished).

The size-dependent free electron damping coefficient might be a function of optical frequency, which has been shown in our previous simulation and in Ref.[29]. Boundary scattering of nanoparticle increases the free electron collision frequency and thus increases the free electron damping. However such collisions might be changed by the optical field force when light irradiates the nanometal. We previously measured the near-infrared and visible absorption spectra of NC thin film containing different types of Al–Al_2O_3 nanoparticles with diameters of 30–110 nm by using an integrating sphere absorption spectrometer.[18] Recently, we have simulated the measured absorption spectra and derived some physical parameters, such as free-electron damping coefficient, of different sized nanometallic Al particles. To explore the influence of the metal core size on the optical absorption property, we obtain approximate relationships of free-electron damping coefficient γ to metal core diameter d and incident optical wavelength λ by fitting the data calculated previously. Figure 1 plots γ versus d at different wavelengths.

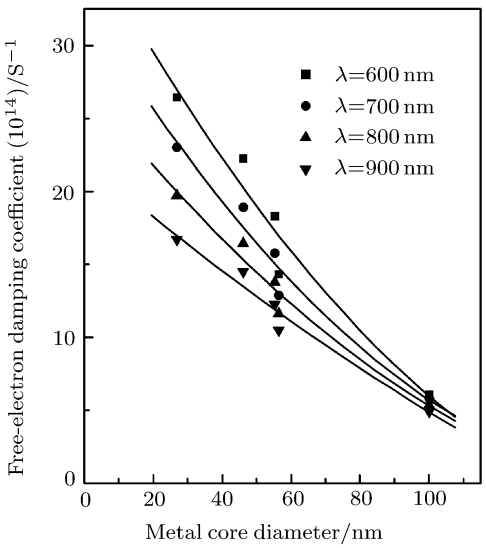


Fig.1. Free-electron damping coefficient against the metal Al-core diameter as determined by our previous simulation of absorption spectra at the optical wavelength 600 (squares), 700 (circles), 800 (upward triangles), and 900 nm (downward triangles). The solid lines are the fitting to the data obtained by simulation.

The symbols represent the values of γ for different sized nanometallic Al-core diameters gained by simulating experiment data of absorption spectra. The solid lines are the fitting curves, which obey the following expression

$$\gamma = b_1(\lambda) - b_2(\lambda)d + b_3(\lambda)d^2, \tag{7}$$

where $b_1(\lambda)$, $b_2(\lambda)$ and $b_3(\lambda)$ are the wavelength-dependent fitting constants. We extract some corresponding data between wavelength and b_1, b_2 and b_3

from the fitting results of Fig.1 and extrapolate out their relationships in Fig.2.

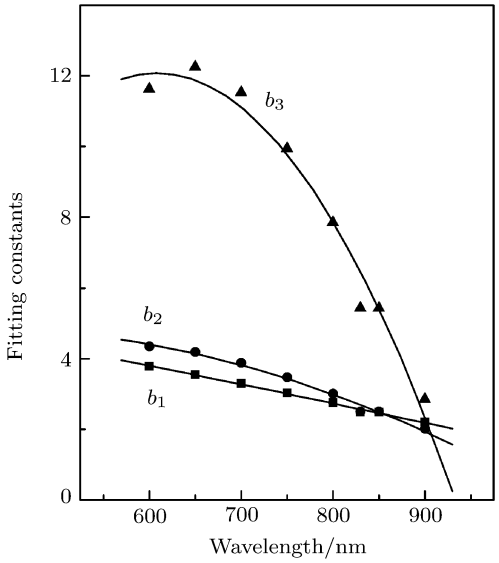


Fig.2. Dependence of the fitting constants b_1, b_2 and b_3 on the wavelength obtained with the help of the fitting relationship in Fig.1 as explained in the text. The solid lines are the fitting for the obtained data.

The fitting formulas are listed as follows:

$$b_1(\lambda) = (6.72 - 0.004\lambda - 5.57 \times 10^{-7}\lambda^2) \times 10^{15},$$
$$b_2(\lambda) = (3.08 + 0.009\lambda - 1.16 \times 10^{-5}\lambda^2) \times 10^{13},$$
$$b_3(\lambda) = (-30.3 + 0.139\lambda - 1.14 \times 10^{-4}\lambda^2) \times 10^{10}, \quad (8)$$

where the unit of λ is nanometer. According to Eqs.(7) and (8), the free-electron damping coefficient can be evaluated by varying the metal core size and incident optical energy. Then, we can calculate the effects of size and shape by using Eqs.(1)–(8).

3. Calculation results and discussions

3.1. Effects of core and shell sizes

Figure 3 clearly reflects the dependence of nanoparticle mass absorption coefficient on nanoparticle dimensions viz Al core radius and Al_2O_3 shell thickness at different optical wavelengths. They are calculated from the spheroidal model, and the total aluminium mass is kept constant. The parameters values in the calculation are listed as follows: $\hbar\omega_P$=15.0 eV,[27] $\hbar\omega_2$=4.83 eV,1) ρ=0.93×10^{-13} S,1) ω_{p1}=1.93×10^{15} S^{-1},1) γ_1=7.60×10^{14} S^{-1},1) ε_2=3.10,[18]

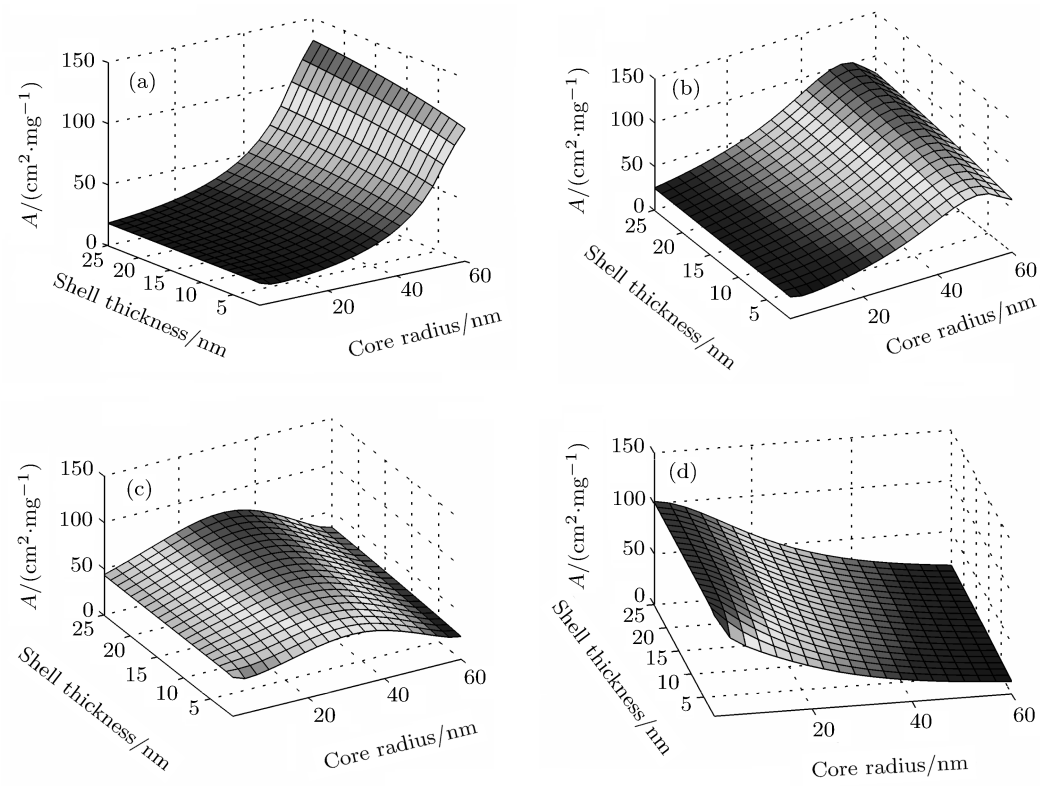


Fig.3. Mass absorption coefficient as a function of Al core radius and oxide shell thickness at optical wavelengths of (a) 750, (b) 850, (c) 900, and (d) 950 nm.

*Those value are Obtained from our previous simulations of absorption spectra in other paper (unpublished)

and ε_m=2.25.[18] It can be seen from Fig.3 that the maximal absorption is determined by core size, shell thickness and incident optical energy. The Al core should be reduced to obtain the maximal absorption when the excited energy is lower. Exactly, metallic core size and excited energy control the holistic absorption characteristic. Fixing the core size, an increase in oxide shell thickness leads to the increase of absorption ability, which is basically due to the increase of nanoparticle dimensions (c_1, c_2, c_3) in Eq.(4). This calculation can be used to predict the desired dimension of nanoparticles with different absorption abilities, or evaluate the absorption ability of given nanoparticles.

3.2. Oxidization effect

Oxidization of nanometallic particle is a special case of changing core and shell sizes. The oxide shell grows at the expense of the wane of Al core. The change seems to be slight but non-negligible for nanoparticles. We calculate the mass absorption coefficients of Al nanoparticles during oxidization as shown in Fig.4. The values of original unoxidized Al diameter (D) are 80 and 120 nm. The excited optical wavelengths are 650, 750, and 900 nm, separately.

As can be seen, the mass absorption coefficient may be changed largely with the decrease of Al core radius, i.e. the increase of oxidization extent. The variation of larger nanoparticle (D=120 nm) is bigger than that of the smaller one (D=80nm). Given that the Al core is oxidized infinitely, the mass absorption coefficient will trend to a constant that is dependent only on the incident optical energy and independent of the initial dimension of nanoparticles. Furthermore, oxidization may increase absorption as can be seen from 120 nm diameter nanoparticle at a 900 nm wavelength. It seems to be a counter-instinctive phenomenon, which shows the oxidization of nanometallic particle does not always hinder the optical absorption.

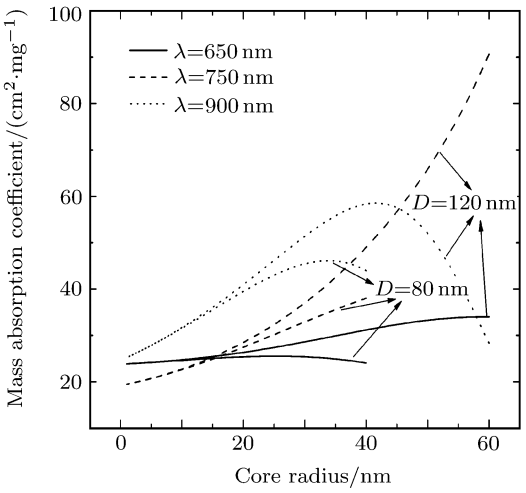


Fig.4. Effect of oxidization on the mass absorption coefficient of aluminium nanoparticles with diameters of 80 and 120 nm at different optical wavelengths. The dotted, dashed, and solid lines correspond to the wavelengths of 900, 750, and 650 nm, respectively.

The same enhancement effect due to oxidization was also derived by Ruppin[20] in far-infrared absorption. However our calculation indicates the enhancement is conditional and dependent on light energy and initial dimension of nanoparticle. In order to illustrate the relationship among oxidization, excited energy, and mass absorption coefficient of core-shell nanoparticles in more detail, we draw the three-dimensional morphologies of the two types of nanoparticles as shown in Fig.5. It can be seen that the absorption peak is slight blue-shift by comparing the case of 120 nm diameter nanoparticle with the case of 80 nm diameter nanoparticle. The optimized oxidization extent can therefore be known to derive the maximal or minimal absorption at the different excited energies.

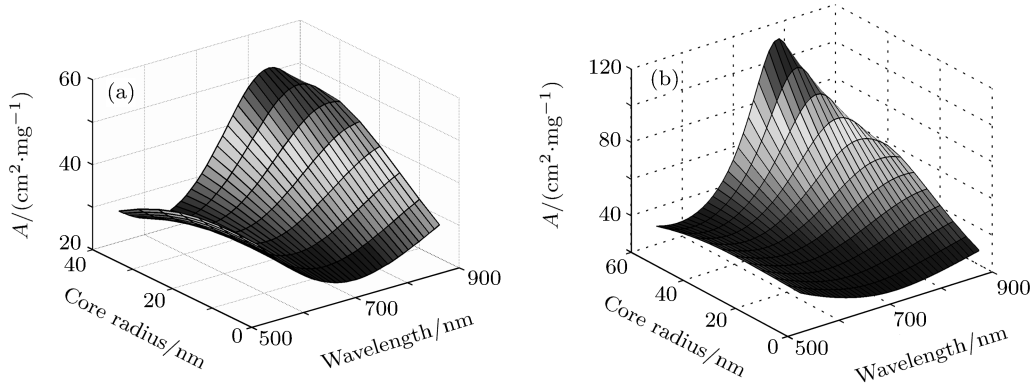


Fig.5. Three-dimensional morphologies corresponding to Fig.4, where panels 5(a) and 5(b) show the effects of oxidation on optical absorption at different excited wavelengths for initial unoxidized nanoaluminium diameters of 80 and 120 nm respectively and the influence dependent on both wavelength and nanoparticle initial dimension.

3.3. Ellipsoidal shape effect

Practically, ellipsoidal nanoparticles immingled in nominal spheroidal nanoparticles are unavoidable. The ellipsoidal shape effect is examined in this part. Figure 6(a) shows the calculated effect of aspect ratio (R), i.e. the ratio of dimension along major axis to that along the minor axis, on the mass absorption coefficient of the Al–Al_2O_3 nanoparticle with an effective diameter of 62.1 nm including a shell thickness of 6 nm.

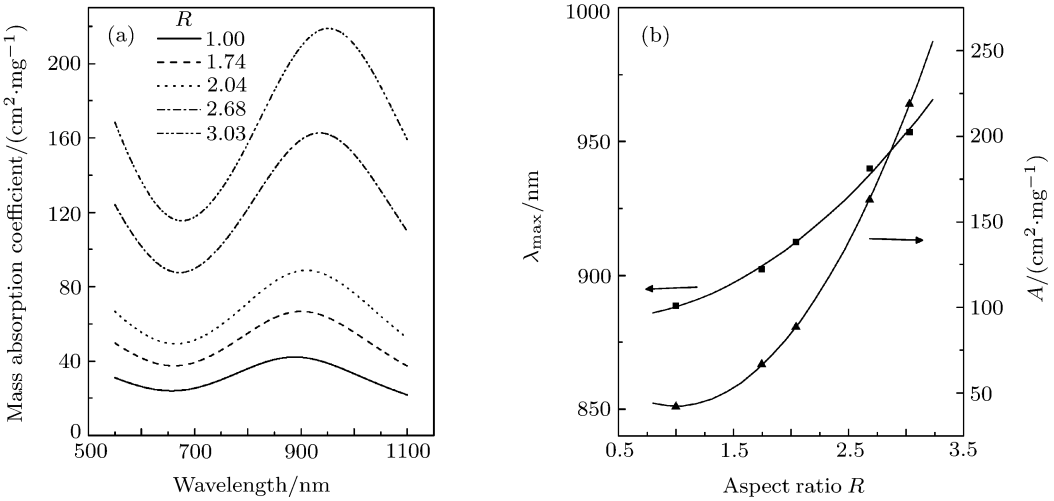


Fig.6. Panel (a) is for the absorption spectra of elongated ellipsoidal nanoparticle calculated from expression (5) with aspect ratio R being variable and the effective diameter of core-shell nanoparticle fixed at 62.1 nm (shell thickness is 6 nm). Panel (b) shows the maximum of the absorption peak position $\lambda_{\max}$ and the maximum of absorption peak intensity A determined from the calculated spectra shown in panel (a) as a function of the aspect ratio R. The solid lines are the fitting curves.

We can see that the larger the aspect ratio is, the larger the mass absorption coefficient will be, which corresponds to the earlier result.[20] The increase can be described by square index relationship ($A = 85.38 - 85.83R + 42.82R^2$) as shown in Fig.6(b). The inter-band absorption peak position $\lambda_{\max}$ shifts toward long wavelengths with squared wavelength, which is also shown in Fig.6(b) ($\lambda_{\max} = 884.83 - 6.26R + 9.67R^2$). The red-shift of absorption peak of metal core-oxide shell nanoparticle generally accords with that of gold nanorods.[36,10] but in latter systems the shift is linear with wavelength. This difference might come from the different materials or nanostructures.

4. Application in nanoenergetic materials

Our calculations could realize their applications in laser igniting nanoenergetic materials. According to Fig.3, two applications could be found. One is that one can predict the used laser ignition frequency when the Al core and Al_2O_3 shell sizes are given according to the practical demand for absorption ability. The other is that core and shell sizes of nanoparticles could be determined to add into energetic materials for obtaining different absorption properties. For example, when the Al-core radius is about 60nm, 750nm ignition wavelength is good for obtaining stronger absorption. If the main output wavelength of laser is 900nm, then nano-Al particle with a radius of about 30nm may be prepared as additives of energetic materials. Sometimes the oxidization of nanometallic particles may be favourable for laser ignition because it can increase the optical absorption. But it should not be oxidized unrestrainedly due to subsequent attenuation as shown in Fig.5. The optimal oxidization point can be found through calculation. From Fig.5, for a 80 nm diameter metallic Al particle, a 5 nm thick oxide layer may be suitable when the excited optical wavelength is 850 nm, and 10 nm oxide shell thickness is good for the 120 nm diameter Al particle at the same optical wavelength. The ellipsoidal nanoadditive is more beneficial for optical absorption than the spheroidal one. It can increase the ignition sensitivity and reduce the ignition time. The suitable relationship among aspect

ratio, optical wavelength, and absorption intensity is distinct from that in Fig.6(a). Therefore these calculations can provide valuable information about the preparation and laser ignition of nanoenergetic materials. The methods are applicable to other similar component nanoenergetic materials.

5. Conclusion

The effects of core dimension, shell thickness, and ellipsoid aspect ratio on the absorption spectra of nanoaluminium particles with oxide coating are investigated theoretically. Some important and valuable results are found. Metal core size and excited optical energy play a dominate role in determining the absorption characteristic. The aluminium core and oxide shell sizes can be determined at different excited energies for deriving different absorption properties by calculation. A counter-instinctive phenomenon is found that the absorption ability can increase due to the metal oxidation. But this enhancement depends on an appropriate incident optical wavelength and a suitable initial nanoparticle dimension as shown in Fig.4. At a constant volume, the absorption property of ellipsoidal nanoparticles is better than that of spheroidal nanoparticles. It can increase the absorption ability and reduce the ignition time of nanoenergetic materials. This predominance is more evident with the increase of ellipsoid aspect ratio. Our calculation program can give a good prediction for designing appropriate physical parameters of nanoadditives such as the core dimension, the shell thickness, and the ellipsoid aspect ratio. The corresponding ignition wavelength can also be determined. These are very helpful for practical applications in laser ignition and nanoenergetic material preparation.

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References

[1] Granier J J and Pantoya M L 2002 *Proceedings of the 2002 8th AIAA/ASME Joint Thermophysics and Heat Transfer Conference* (AIAA/ASME, St. Louis, Missouri) p3030
[2] Yang Y Q, Wang S F, Sun Z Y and Dlott D D 2004 *Appl. Phys. Lett.* **85** 1493
[3] Schoenitz M and Dreizin E 2004 *J. Propul. Pow.* **20** 1064
[4] Yang Y Q, Sun Z Y, Wang S F and Dlott D D 2003 *J. Phys. Chem.* B **107** 4485
[5] Pantoya M L and Granier J J 2005 *Propellents, Explosives, Pyrotechnics* **30** 53
[6] Bourne N K 2001 *Proc. R. Soc. Lond.* A **457** 1401
[7] Granier J J and Pantoya M L 2004 *Combust. Flame* **138** 373
[8] Sosa I O, Noguez C and Barrera R G 2003 *J. Phys. Chem.* B **107** 6269
[9] Chen X Y, Cui H, Liu P and Yang G W 2007 *Appl. Phys. Lett.* **90** 183118
[10] Jain P K, Lee K S, Ei-Sayed I H and Ei-Sayed M A 2006 *J. Phys. Chem.* B **110** 7238
[11] Liu X F, Jiang C Z, Ren F and Fu Q 2005 *Acta Phys. Sin.* **54** 4633 (in Chinese)
[12] Sun Z Q, Cai Q and Song X P 2006 *Chin. Phys.* **15** 0859
[13] Taton T A, Mirkin C A and Letsinger R L 2000 *Science* **289** 1757
[14] Yang J, Lee J Y and Too H P 2005 *J. Phys. Chem.* B **109** 19208
[15] Kim F, Song J H and Yang P 2002 *J. Am. Chem. Soc.* **124** 14316
[16] Zhao L Y, Gao F, Wang Z B, Ming H and Xu X L 2007 *Acta Phys. Sin.* **56** 3564 (in Chinese)
[17] Shen H, Cheng B L, Lu G Q, Wang W T, Guan D Y, Chen Z H and Yang G Z 2005 *Chin. Phys.* **14** 1915
[18] Yang Y Q, Wang S F, Sun Z Y and Dlott D D 2005 *Propellents, Explosives, Pyrotechnics* **30** 171
[19] Wang S F, Yang Y Q, Yu H and Dlott D D 2005 *Propellents, Explosives, Pyrotechnics* **30** 148
[20] Ruppin R 1979 *Phys. Rev.* B **19** 1318
[21] Simanek E 1977 *Phys. Rev. Lett.* **38** 1161
[22] Palik E D 1985 *Handbook of Optical Constants of Solids* (New York: Academic) p369
[23] Hubenthal F, Hendrich C, Ouacha H, Blazquez-Sanchez D and Trager F 2005 *Int. J. Mod. Phys.* B **19** 2604
[24] Moskovits M, Srnova-Sloufova I and Vlckova B 2002 *J. Chem. Phys.* **116** 10435
[25] Rojas R and Claro F 1988 *Phys. Rev.* B **37** 6799
[26] Wang W G, Yang G, Guan D Y, Wu W D and Chen Z H 2004 *Acta Phys. Sin.* **53** 932 (in Chinese)
[27] Bohren F and Huffman D R 1983 *Absorption and Scattering of Light by Small Particles* (New York: Wiley) p149
[28] Liu J S, Li R X, Zhu P P, Xu Z Z and Liu J R 2001 *Acta Phys. Sin.* **50** 1121 (in Chinese)
[29] Taneja P and Ayyub P 2002 *Phys. Rev.* B **65** 245412
[30] See K C, Spicer J B, Brupbacher J, Zhang D J and Vargo T G 2005 *J. Phys. Chem.* B **109** 2693
[31] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 *J. Phys. Chem.* B **107** 668
[32] Aden A L and Kerker M 1951 *J. Appl. Phys.* **22** 1242
[33] Li W H, Yang C C, Tsao F C, Wu S Y, Huang P J, Chung M K and Yao Y D 2005 *Phys. Rev.* B **72** 214516
[34] Sun C Q, Chen T P, Tay B K, Li S, Huang H, Zhang Y B, Pan L K, Lau S P and Sun X W 2001 *J. Phys.* D: *Appl. Phys.* **34** 3470
[35] http://netclass.csu.edu.cn/jpkc2006/ziyuan/jiaoan/jg09.htm
[36] Link S, Mohamed M B and EI-Sayed M A 1999 *J. Phys. Chem.* B **103** 3073