Partial electrical potential distribution around nanospheres in metallic nanostructured films*

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(Received 19 July 2011; revised manuscript received 15 August 2011)

In light of the nanostructured surface model, where half-spherical nanoparticles grow out symmetrically from a plane metallic film, the mathematical model for the partial electrical potential around nanospheres is developed when a uniform external electric field is applied. On the basis of these models, the three-dimensional spatial distribution of the partial electrical potential is obtained and given in the form of a curved surface using a numerical computation method. Our results show that the electrical potential distribution around the nanospheres exhibits an obvious geometrical symmetry. These results could serve as a reference for investigating many abnormal phenomena such as abnormal infrared effects, which are found when CO molecules are adsorbed on the surface of nanostructured transition metals.

Keywords: partial electrical potential, nanosphere, metallic nanostructured film

PACS: 78.67.–n, 82.45.Yz, 61.46.–w **DOI:** 10.1088/1674-1056/21/1/017807

1. Introduction

Nanostructured films of transition metals and alloys are widely used as nanosensors, nanoelectrodes and electrocatalysts for direct fuel cells.[1−4] The optical properties of metallic nanostructured film materials have been an active research topic in recent years.[5−10] It has been reported that when CO molecules are adsorbed on a nanostructured transition metal surface, abnormal infrared absorption behaviours can be observed. When the nanoparticles grow to a certain size on the surfaces of some nanostructured platinum-group metal films, enhanced asymmetric line shapes of anti-absorption – rather than Gaussian-type spectral line shapes – have been found,[11] some of which can be classified as Fano-like line shapes.[12,13] It is also observed that once the nanoparticles agglomerate, the line shape exhibits enhanced anti-absorption with an increased bandwidth. These anti-absorption phenomena are known as abnormal infrared effects (AIREs), and have been observed in various platinum-group metals such as platinum and rhodium.[14] It is universally acknowledged that the formation mechanism of AIREs is rather complicated and that there is no mature reference theory so far. The previous investigations pointed out that the infrared spectral line shape is determined by the molecular polarizability.[15,16] However, the molecular polarizability is related to the interactions between adsorbed molecules and the local electric field, and between adsorbed molecules and the nanostructured metallic substrate.[16] Theoretically, the interactions and then the molecular polarizability can be obtained by computing the partial electrical potential around the nanoparticles that grow out from the nanostructured film surface. On the other hand, when the nanostructured film is used for nanosensors or nanoelectrodes, the electrical potential around the nanoelectrode is an important parameter, which is significant for investigating electron mobility and charge transport between the nanoparticles. In other words, partial electrical potential plays an important role in investigating the physical properties of the nanostructured films. Based on the nanostructured surface model, in which the metallic half-spherical nanoparticle array (monolayer) grows out from a plane film with a six-fold spatial symmetry, in the present paper we develop a mathematical model for the partial electrical potential around the nanospheres, so the three-dimensional spatial distribution of the electrical potential can be obtained and shown in the form of a curved surface by a numerical computation method.

*Project supported by the Natural Science Foundation of Fujian Province, China (Grant No. 2010J01210).

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2. Theoretical model

Consider a nanostructured film composed of an array of half-spherical nanoparticles growing out from a grounded metal plane in a two-dimensional hexagonal configuration. An external electric field, E_0, is applied in the direction normal to the film surface, as shown in Fig. 1(a). If the number of nanoparticles is large enough, it is reasonable to treat them in an identical manner, since all the nanoparticles are electrically equivalent to each other. In order to index the position of each nanoparticle, for convenience we use a non-orthogonal $2\pi/3$ coordinate system with its origin fixed at the centre of one of the nanoparticles, as shown in Fig. 1(b).

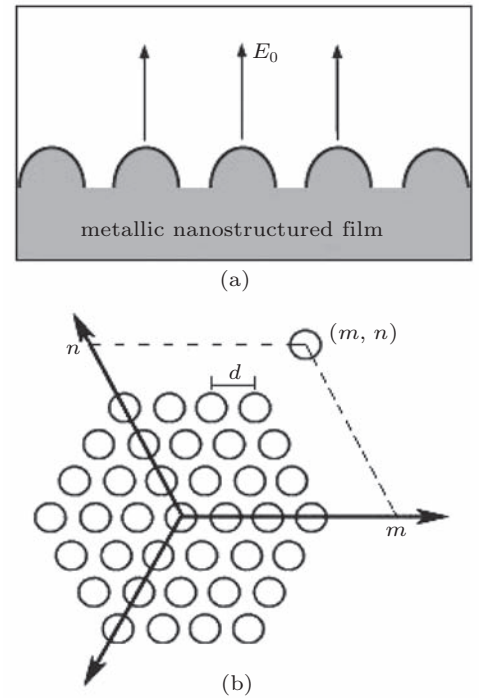


Fig. 1. (a) A metallic nanostructured film with the nanospheres in a uniform external electric field, and (b) a hexagonal array of nanospheres and the non-orthogonal $2\pi/3$ coordinate system.

Obviously, the proposed problem is a three-dimensional electrostatic problem with geometrical symmetry. Since there is no free charge in the upper space, the electrical potential distribution ψ satisfies the Laplace equation

$$\nabla^2\psi = 0. \tag{1}$$

Equation (1) is restrained by the boundary condition that the nanostructured film is grounded, i.e. the electrical potential equals zero for all the nanospheres. If we use the spherical coordinate system, the electrostatic boundary condition is given by

$$\psi = \begin{cases} -E_0 r\cos\theta, & (r \to \infty), \\ 0, & (r = R_0), \end{cases} \tag{2}$$

where R_0 is the radius of the nanosphere and r is the distance from the position of the field point to the origin. Since the geometrical symmetry of the electrical field distribution (assume in the z direction), the electrical potential around the nanospheres can be expressed as

$$\psi = \sum_{k,l} \left(a_{kl} r^k + \frac{b_{kl}}{r^{k+1}} \right) \mathrm{P}_k^l(\cos\theta)\cos l\varphi, \tag{3}$$

where a_{kl} and b_{kl} are undetermined coefficients, and P_k^l is the associated Legendre polynomial. It should be pointed out that we are concerned only with the electrical potential around the nanospheres, and the electrical field that exists far away from the nanospheres is not taken into account. Therefore, a few lower order terms of the linear superposition in Eq. (3) can approximate the solution of the partial electrical potential. And furthermore, in view of the six-fold symmetry of the nanosphere array, the linear superposition of the electrical potential distribution should also be of six-fold symmetry. Then the approximate solution can be expressed as

$$\begin{aligned} \psi = & -E_0 r\cos\theta + b_1 \sum_{m,n} \frac{\cos\theta_{mn}}{r_{mn}^2} \\ & + b_2 \sum_{m,n} \frac{\mathrm{P}_3(\cos\theta_{mn})}{r_{mn}^4} + b_3 \sum_{m,n} \frac{\mathrm{P}_5(\cos\theta_{mn})}{r_{mn}^6} \\ & + b_4 \sum_{m,n} \frac{\mathrm{P}_7(\cos\theta_{mn})}{r_{mn}^8} \\ & + b_5 \sum_{m,n} \frac{\mathrm{P}_7^6(\cos\theta_{mn})\cos 6\varphi_{mn}}{r_{mn}^8}, \end{aligned} \tag{4}$$

where subscripts (m, n) represent the position of the nanosphere, and r_{mn}, θ_{mn} and φ_{mn} denote the distance, the polar angle and the azimuthal angle with respect to nanosphere (m, n), respectively, which can be determined by spherical coordinates r, θ, φ and (m, n) based on the geometrical relations. The Legendre polynomials with even degrees are not taken into account due to the symmetry of the system. $\mathrm{P}_7^6(\cos\theta_{mn})$ is an associated Legendre polynomial. The sixth term of expression (4) is taken into account due to the six-fold symmetry of the nanosphere array. Numerical coefficients b_1–b_5 are determined by the boundary conditions for the contributions of terms 2–6 in expression (4), respectively.

3. Equipotential surface features

For the present numerical computation, we assume that the radius of each nanosphere is $R_0 = 5$ nm (and 7.5 nm) and the distance between two adjacent nanospheres is $d = 15$ nm. A total of 1141 identical nanospheres in a two-dimensional hexagonal array are considered, which correspond to subscripts $(m, n)_{\max} = (20, 20)$ in Fig. 1(b). The external electric field is $E_0 = 6 \times 10^6$ V/m, which is applied in the normal direction of the nanostructured film. After numerical coefficients b_1–b_5 of expression (4) are determined with boundary condition (2), the electrical potential around the nanospheres can be obtained. According to expressions (2) and (4), we obtain the numerical coefficients b_1–b_5 listed in Table 1.

Table 1. The b_1–b_5 coefficients in expression (4).

R_0/nm	d/nm	$b_1/10^{-1}$	$b_2/10^{-2}$	$b_3/10^{-3}$	$b_4/10^{-4}$	$b_5/10^{-8}$
5.0	15.0	7.18	2.94	–3.67	4.52	9.12
7.5	15.0	7.05	2.86	–3.77	4.43	9.08

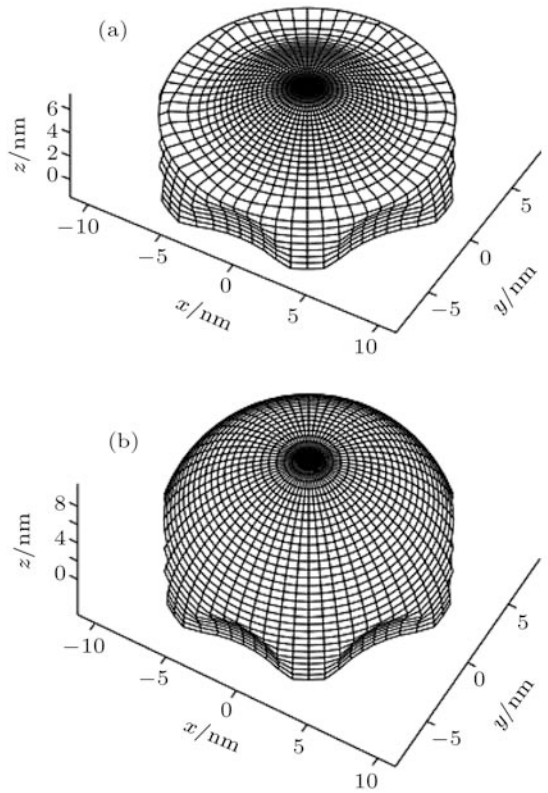


Fig. 2. The top views of the equipotential surfaces for electrical potentials equaling: (a) −0.01 V and (b) −0.05 V.

Since all nanospheres are electrically equivalent to each other, the electrical potential can therefore be computed by expression (4) for all space points around any nanosphere. The top and bottom views of the equipotential surfaces for two given electrical potential values are shown in Figs. 2 and 3, respectively, and are centred around the symmetrical axis of a nanosphere. They exhibit partial electrical potential distribution around one nanosphere. From Figs. 2 and 3 we can clearly see that the shapes of the equipotential surfaces are different for different electrical potential values. The closer to the nanosphere they are, the flatter they are. However, they are symmetrical and hexagonal due to the symmetry of the array of nanospheres. At the junction of the two nanospheres, the equipotential surfaces become more crooked.

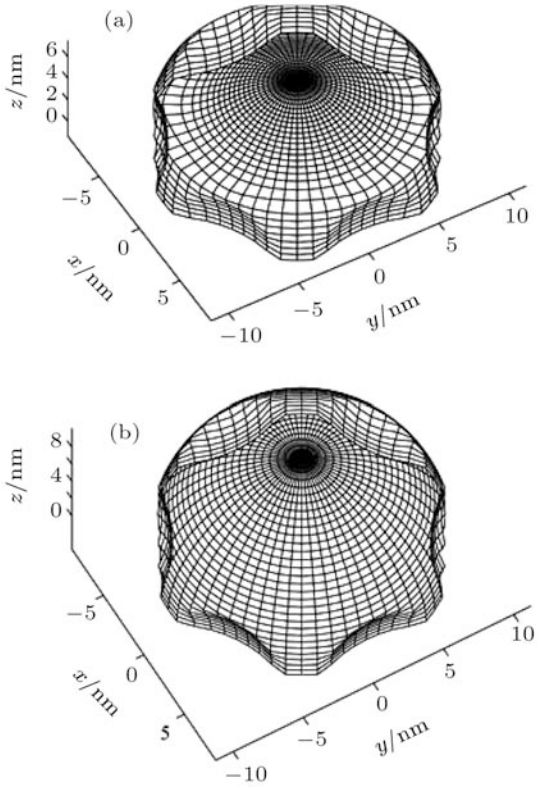


Fig. 3. The bottom views of the equipotential surfaces for electrical potentials equaling: (a) −0.01 V and (b) −0.05 V.

4. Partial electrical potential distribution

Compared with the equipotential surfaces, partial electrical potential distribution at space points around any nanosphere should be more significant for the investigation of the nanostructured film. Figure 4 shows the three-dimensional electrical potential distributions in two given horizontal planes (x–y plane) above the nanostructured film, which are centred around the symmetrical axis of a nanosphere. From Fig. 4, we

can see again that both electrical potential distributions exhibit six-fold symmetry.

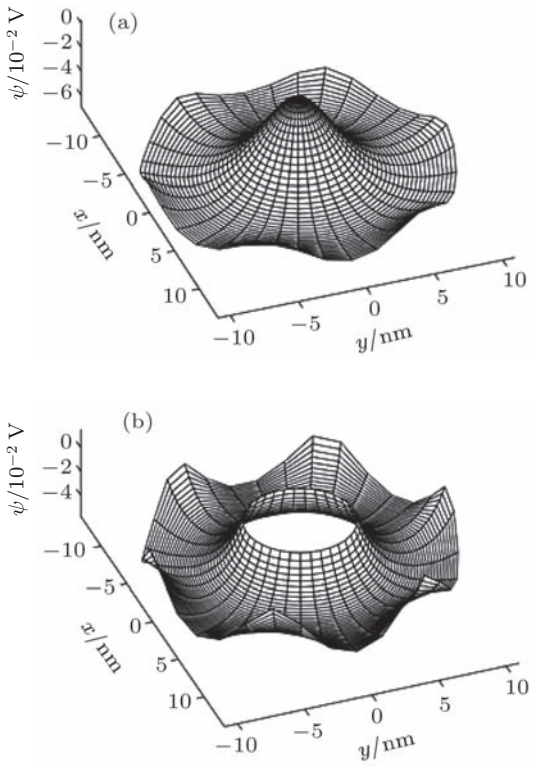


Fig. 4. Partial electrical potential distributions at horizontal planes (a) 5.0 nm and (b) 3.0 nm above the nanostructured film.

5. Conclusion

Metallic nanostructured films have been investigated widely in many fields, such as scanning electron microscopy, microelectrodes and nano spectroscopy. The AIRE is a kind of abnormal phenomenon found in surface physics. In order to theoretically understand the formation mechanism of AIRE, equipotential surfaces for given electrical potential values and partial electrical potential distributions around spherical nanoparticles are obtained when an external electric field is applied to the nanostructured film formed with a nanosphere array. Our computational results show that electrical potential distribution exhibits an obvious variation in a narrow range and an obvious geometrical symmetry. These results are useful for investigating various physical properties of nanostructured films, such as AIREs.

References

[1] Kim J H, Kang G, Nam Y and Choi Y K 2010 *Nanotechnology* **21** 085303
[2] Ioroi T, Yasuda K, Siroma Z, Fujiwara N and Miyazaki Y 2002 *J. Power Source* **112** 583
[3] Lindström R W, Seidel Y E, Jusys Z, Gustavsson M, Wickman B, Kasemo B and Behm R J 2010 *J. Electroanal. Chem.* **664** 90
[4] Niu Z Q, Ma W J, Dong H B, Li J Z and Zhou W Y 2011 *Chin. Phys.* B **20** 028101
[5] Fu J X, Hua Y L, Chen Y H, Liu R J, Li J F and Li Z Y 2011 *Chin. Phys.* B **20** 037806
[6] Guan Z Q, Yutaka A, Jiang D H, Lin H, Yoshitake Y and Wu C X 2004 *Chin. Phys.* **13** 105
[7] Kim S W and Kim S 2001 *Phys. Rev.* B **63** 212301
[8] Lin W G, Sun S G, Zhou Z Y, Chen S P and Wang H C 2002 *J. Phys. Chem.* B **106** 11778
[9] Pinchuk A, Kreibig U and Hilger A 2004 *Surf. Sci.* **557** 269
[10] Chou K C, Westerberg S, Shen Y R, Ross P N and Somorjai G A 2004 *Phys. Rev.* B **69** 153413
[11] Chen W, Sun S G, Zhou Z Y and Chen S P 2003 *J. Phys. Chem.* B **107** 9808
[12] Patthey F, Schaffner M H, Schneider W D and Delley B 1999 *Phys. Rev. Lett.* **82** 2971
[13] Ujsaghy O, Kroha J, Szunyogh L and Zawadowski A 2000 *Phys. Rev. Lett.* **85** 2557
[14] Huang X J, He S Z and Wu C X 2006 *Chin. Phys.* **15** 2389
[15] Crljen Z and Langreth D C 1987 *Phys. Rev.* B **35** 4224
[16] Huang X J , Wu C X, Chen Y J, Lin H, Jiang D H and Sun S G 2005 *Acta Phys. Sin.* **54** 429 (in Chinese)