Electric potential distribution near nanocone arrays on metal substrates*

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(Received 17 November 2011; revised manuscript received 24 November 2011)

Based on the nanostructured surface model, where conical nanoparticle arrays grow out symmetrically from a plane metal substrate, a theoretical model of the local electric potential near nanocones is built when a uniform external electric field is applied. In terms of this model, the electric potential distribution near the nanocone arrays is obtained and given by a curved surface using a numerical computation method. The computational results show that the electric potential distribution near the nanocone arrays exhibit an obvious geometrical symmetry. These results could serve as a basis for explaining many abnormal phenomena, such as the abnormal infrared effects (AIREs) which are found on nanostructured metal surfaces, as well as a reference for investigating the applications of nanomaterials, such as nanoelectrodes and nanosensors.

Keywords: nanocone arrays, nanostructured metal surface, electric potential distribution

PACS: 78.67.–n, 82.45.Yz, 61.46.–w **DOI:** 10.1088/1674-1056/21/5/057802

1. Introduction

Recently, much attention has been paid to the physical and chemical properties of metal nanostructured film materials in physics, chemistry, material science, surface science, and so on. It has been found that when some gas (e.g., carbon monoxide) molecules are adsorbed on a nanostructured transition metal surface, the infrared absorption exhibits some abnormal phenomena, such as the shift and enhancement of the spectral line,[1−4] and even the appearance of an anti-absorption peak, which is known as the abnormal infrared effect (AIRE).[5,6] It is universally received that the intrinsic mechanism of AIRE is so complicated that there has been no mature theory that can explain these phenomena so far. Previous research has reported that the shape of the infrared spectral line is determined by the imaginary part of molecular polarizability.[7−10] However, molecular polarizability is closely related to the local electric potential near the nanoparticles. Theoretically, molecular polarizability can be obtained in terms of the local electric potential near the nanoparticles, so the computation of local electric potential has become an important way to investigate the mechanism of AIRE. On the other hand, in recent years, the nanostructured film of transition metals or alloys has been widely used in nanosensors, nanoelectrodes and electrocatalysts for direct fuel cells.[11−14] Recently, it has been reported that the Oak Ridge team, led by Xu *et al.*[15] of ORNL (Oak Ridge National Laboratory) developed a three-dimensional (3D) solar cell platform based on a nanoconical film, which can improve carrier transport properties and enhance the photoelectric conversion efficiency to nearly 80%. Machado *et al.*[16] also studied the electric field properties of nanoconical structures. In these investigations, the local electric potential of the nanoconical electrode is an important parameter, which is significant for charge transport between the nanoelectrodes. In the present paper, based on the nanostructured surface model where metal nanocone arrays (monolayers) grow out into sixfold symmetry from a plane film substrate, a mathematical model of the local electric potential near the nanocones is built, so the 3D spatial distribution of the electric potential is obtained by a numerical computation method and shown in the form of a curved surface. These results may serve as a basis for further relevant investigations.

2. Theoretical model

Suppose that the identical conical nanoparticle arrays grow out symmetrically from a grounded metal-

*Project supported by the Natural Science Foundation of Fujian Province, China (Grant Nos. 2010J01210, B509043A, and 2011J05006).

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lic substrate, and an external uniform electric field $\boldsymbol{E}_0$ is applied in the direction normal to the substrate, as shown in Fig. 1. The number of nanocones is large enough so that all nanocones can be treated as being electrically equivalent to each other.

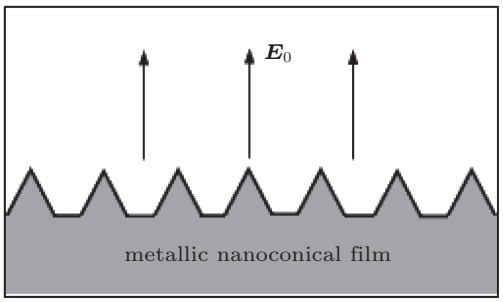


Fig. 1. A metallic nanostructured film with nanocones in a uniform external electric field.

Considering a nanocone array in a two-dimensional (2D) hexagonal configuration, as shown in Fig. 2(a), we use a non-orthogonal $2\pi/3$ coordinate system with its origin fixed at the centre of one of the nanocones, and denote the position of each nanocone by (m, n). In order to investigate the electric potential distribution near a metallic nanocone with conical angle 2α, as shown in Fig. 2(b), the spherical coordinate system is used, and the angular ranges of free space are $0 \leq \theta \leq \beta$, $0 \leq \varphi \leq 2\pi$, $\beta = \pi - \alpha$. This is a 3D electrostatic problem with geometrical symmetry. The boundary condition that the nanostructured substrate is grounded is assumed, so the electrical potential equals zero for all the nanocones. Because of the space symmetry in the electric potential distribution, the electric potential can be expressed as

$$\Psi(r, \theta) = R(r)\mathrm{P}(\theta), \tag{1}$$

and the electrostatic boundary condition is given by

$$\Psi(r, \theta) = 0, \quad (\theta = \beta). \tag{2}$$

Substitute Eq. (1) into Laplace's equation, then we will have

$$R(r) = Ar^l + Br^{-(l+1)}, \tag{3}$$

where A and B are undetermined constants. $\mathrm{P}(x)$ $(x = \cos\theta)$ satisfies Legendre's equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[(1-x^2)\frac{\mathrm{dP}}{\mathrm{d}x}\right] + l(l+1)\,\mathrm{P} = 0. \tag{4}$$

Since the space points of interest are in an angular range of $\cos\beta \leq x \leq \cos 0°$, $\mathrm{P}(x)$ must be a regular function when $x = \cos 0° = 1$. Therefore, the solution of Eq. (4) must be expanded into a power series solution for $x = 1$. Now let $y = (1-x)/2$, then Eq. (4) will become

$$\frac{\mathrm{d}}{\mathrm{d}y}\left[y(1-y)\frac{\mathrm{dP}}{\mathrm{d}y}\right] + \lambda(\lambda+1)\,\mathrm{P} = 0. \tag{5}$$

Note that we substitute λ for l in Eq. (4) and Eq. (3) because the λ is no longer an integer as l. The power series solution of Eq. (5) is defined as

$$\mathrm{P}(y) = \sum_{k=0}^{\infty} a_k y^k. \tag{6}$$

Substitute Eq. (6) into Eq. (5), and the recurrence relation for the coefficients of the series will be given by

$$a_{k+1}/a_k = (k-\lambda)(k+\lambda+1)/(k+1)^2. \tag{7}$$

Let $a_0 = 1$ (normalization), and use the relation of $y = (1-x)/2$, then Eq. (5) will be expressed as

$$\begin{aligned}\mathrm{P}_\lambda(x) = 1 &+ \frac{(-\lambda)(\lambda+1)}{1\,!\,1\,!}\,[(1-x)/2] + \frac{(-\lambda)(-\lambda+1)(\lambda+1)(\lambda+2)}{2\,!\,2\,!}\,[(1-x)/2]^2 + \cdots \\ &+ \frac{(-\lambda)(-\lambda+1)\cdots(-\lambda+k-1)(\lambda+1)(\lambda+2)\cdots(\lambda+k)}{k\,!\,k\,!}\,[(1-x)/2]^k + \cdots\end{aligned} \tag{8}$$

Since the electric potential must be a finite value at the coordinate origin ($r = 0$), we have $B = 0$ in Eq. (3). Thus, from Eqs. (1) and (3), the basic solution of electric potential is given by

$$\Psi = Ar^\lambda \mathrm{P}_\lambda(x) = Ar^\lambda \mathrm{P}_\lambda(\cos\theta).$$

According to the boundary condition Eq. (2), we have

$$\mathrm{P}_\lambda(\cos\beta) = 0. \tag{9}$$

For a given β, in general, there are values of infinite λ satisfying Eq. (9), i.e., λ_i $(i = 1, 2, 3, \ldots)$ which constitute an eigenvalue sequence. When $\lambda = \lambda_i$, $\cos\beta$ is the i-th zero point of $\mathrm{P}_\lambda(\cos\beta)$.

According to the superposition principle of electric potential, the complete solution of Eq. (1) should be the linear superposition of the basic solutions. Since we are concerned only with the characteristics of

electric potential near the nanocones, and the electrical potential that exists far from the nanocones is not taken into account, only a few lower order items of the complete solution are enough to approximate to the accurate solution of local electric potential. Furthermore, in view of the six-fold symmetry of the nanocone arrays, the linear superposition of the local electric potential distributions should also be of six-fold symmetry. Then the approximate solution of Eq. (1) can be expressed as

$$\begin{aligned}\Psi = & -E_0 r\cos\theta + a_1\sum_{m,n}\left(\frac{r_{mn}}{R}\right)^{\lambda_1}\mathrm{P}_{\lambda_1}(\cos\theta_{mn}) \\ & + a_2\sum_{m,n}\left(\frac{r_{mn}}{R}\right)^{\lambda_2}\mathrm{P}_{\lambda_2}(\cos\theta_{mn}) \\ & + a_3\sum_{m,n}\left(\frac{r_{mn}}{R}\right)^{\lambda_3}\mathrm{P}_{\lambda_3}(\cos\theta_{mn}) \\ & + a_4\sum_{m,n}\left(\frac{r_{mn}}{R}\right)^{\lambda_4}\mathrm{P}_{\lambda_4}(\cos\theta_{mn}) \\ & + a_5\sum_{m,n}\left(\frac{r_{mn}}{R}\right)^{\lambda_6}\mathrm{P}^6_{\lambda_6}(\cos\theta_{mn})\cos 6\varphi_{mn}, \quad (10)\end{aligned}$$

where R is the bottom radius of the nanocone; $\mathrm{P}^6_{\lambda_6}(\cos\theta_{mn})$ denotes the non-integer-order associated Legendre function, which is taken into account due to the six-fold symmetry in the electric potential distribution; r_{mn}, θ_{mn}, and φ_{mn} denote the distance, the polar angle, and the azimuthal angle of the position of interest (m, n) in Fig. 2(a), respectively, which can be determined by spherical coordinates r, θ, φ, and (m, n) based on geometrical relations. The undetermined coefficients a_1–a_5 are determined by the boundary condition for the contributions of 2^{th}–6^{th} terms in Eq. (10).

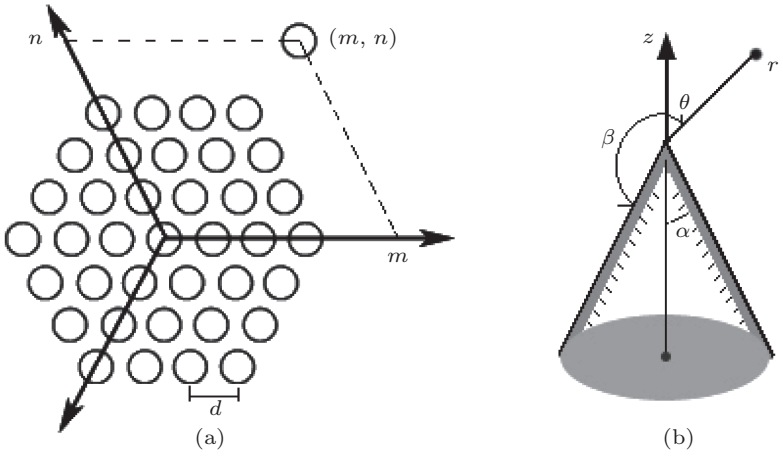


Fig. 2. (a) Hexagonal nanocone arrays and the non-orthogonal $2\pi/3$ coordinate system, and (b) the nanocone and spherical coordinate system.

3. Results and discussion

From Eqs. (8) and (9), the values of λ_i corresponding to the preceding six zero points of the non-integer-order Legendre function are obtained as $\lambda_1 = 0.346$, $\lambda_2 = 1.568$, $\lambda_3 = 2.778$, $\lambda_4 = 3.983$, $\lambda_5 = 5.186$, and $\lambda_6 = 6.388$ for conical angle $2\alpha = 30°$. Then, based on the boundary condition expression (2), the undetermined coefficients a_1–a_5 of Eq. (10) can be obtained. Table 1 gives the computational results for two different geometrical parameters. After the coefficients a_1–a_5 are determined, the local electric potential near the nanocones can be computed from Eq. (10). The parameters of the two geometric structures in the present numerical computation are as follows: the bottom radius of each nanocone $R = 5.0$ nm and $R = 10.0$ nm, the distance between two adjacent nanocones $d = 15.0$ nm and $d = 30.0$ nm, the conical angle $2\alpha = 30°$ and $2\alpha = 15°$, a total of 1141 identical nanocones under consideration, which correspond to the subscripts $(m, n)_{\max} = (20, 20)$ in Fig. 2(a), and the external electric field $E_0 = 6 \times 10^6$ V/m.

Table 1. Coefficients $a_1 - a_5$ in Eq. (10).

R/nm	d/nm	$a_1/10^{-1}$	$a_2/10^{-3}$	$a_3/10^{-4}$	$a_4/10^{-6}$	$a_5/10^{-10}$
5.0	15.0	5.32	–4.27	1.15	–1.03	–9.93
10.0	30.0	4.79	–3.22	4.39	–1.09	15.05

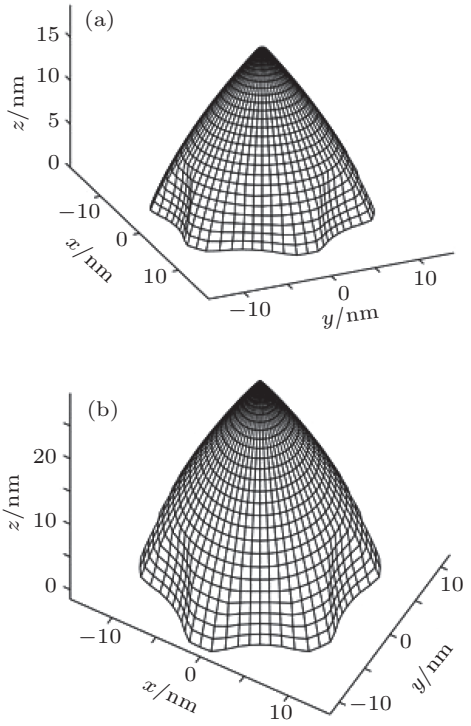


Fig. 3. Top views of the equipotential surfaces for two given values. (a) The electrical potential is −0.04 V, (b) the electric potential is −0.10 V.

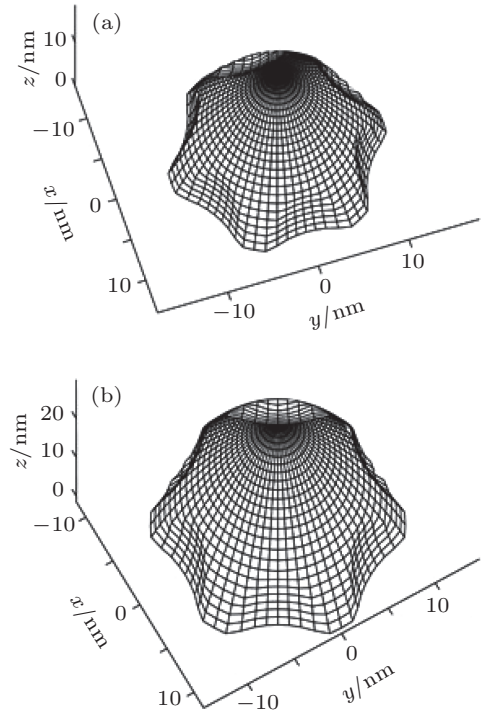


Fig. 4. Bottom views of the equipotential surfaces for two given values. (a) The electrical potential is −0.04 V, (b) the electric potential is −0.10 V.

Since all nanocones are electrically equivalent to each other, the electric potential of all spatial points near any nanocone can be obtained by Eq. (10). The top views of the equipotential surfaces for two given electrical potential values (−0.04 V and −0.10 V) are shown in Figs. 3(a) and 3(b), respectively, and are centred around the symmetrical axis of a nanocone. Figures 4(a) and 4(b) are the bottom views corresponding to Figs. 3(a) and 3(b), respectively.

It can be seen from Figs. 3 and 4 that the equipotential surfaces around the nanocones are axially symmetric. At the junction of two nanocones, the equipotential surfaces become more crooked, which shows hexagonal symmetry due to the symmetrical array of nanocones on the metal substrate.

In contrast with the equipotential surface, the electric potential distribution of the arbitrary horizontal plane above the substrate is another intuitive view of electric potential distribution, and should be more significant for the application investigation of nanostructured material. Figures 5(a) and 5(b) show the 3D electric potential distributions in two given horizontal planes (x–y plane), in which the ordinate represents the electrical potential value at point (x, y). It can be seen from Fig. 5 that the electric potential distribution near a nanocone exhibits an obvious six-fold symmetry, which is an expected result.

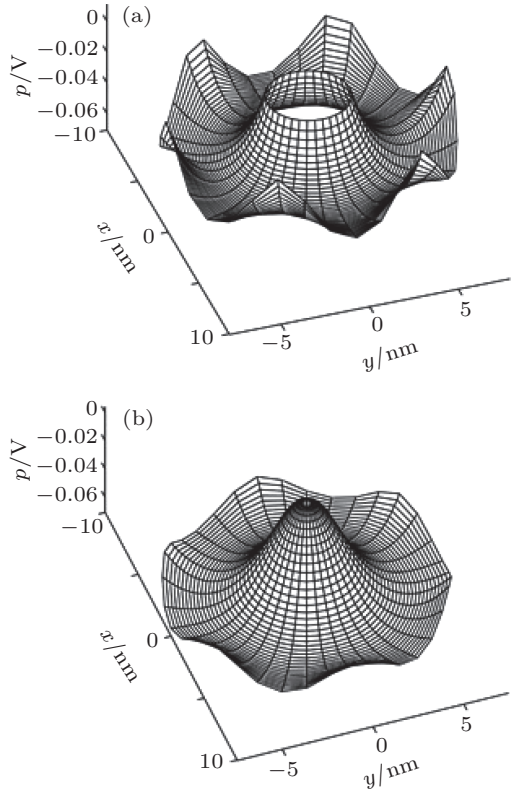


Fig. 5. Local electric potential distributions for two given horizontal planes above the nanostructured substrate. (a) The height 8 nm below the top of the cone, and (b) the height at the level of the top of the cone.

4. Conclusion

The metallic nanostructured film materials widely used in nanoelectrodes, scanning electron microscopy (SEM), nano-spectroscopy, and many other related fields are investigated in this paper. The mechanism of abnormal phenomena with respect to nanostructured materials such as AIREs is rather complicated and requires further exploration. In order to theoretically investigate the characteristics of the electric field near the nanoparticle surface for various nanostructured film materials, the spatial distribution of the local electric potential near the nanocone is given by a numerical computation method and shown in the form of a curved surface. The computational results show that the local electric potential distribution exhibits an obvious variation within a narrow range and an obvious geometrical symmetry, which are consistent with the expected results. These results are helpful for investigating the electrical properties of various nanostructured film materials.

References

[1] Wang Q Q and Zhao T Y 1999 *Acta Phys. Sin.* **48** 539 (in Chinese)

[2] Kim S W and Kim S 2001 *Phys. Rev.* B **63** 212301

[3] Chen W, Sun S G, Zhou Z Y and Chen S P 2003 *J. Phys. Chem.* B **107** 9808

[4] Pinchuk A, Kreibig U and Hilger A 2004 *Surf. Sci.* **557** 269

[5] Lin W G, Sun S G, Zhou Z Y, Chen S P and Wang H C 2002 *J. Phys. Chem.* B **106** 11778

[6] Huang X J, He S Z and Wu C X 2006 *Chin. Phys.* **15** 2389

[7] Crljen Z and Langreth D C 1987 *Phys. Rev.* B **35** 4224

[8] 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)

[9] Zhu B H, Wang F F, Zhang K, Ma G H, Guo L J and Qian S X 2007 *Acta Phys. Sin.* **56** 4024 (in Chinese)

[10] 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

[11] Kim J H, Kang G, Nam Y and Choi Y K 2010 *Nanotechnology* **21** 085303

[12] Ioroi T, Yasuda K, Siroma Z, Fujiwara N and Miyazaki Y 2002 *J. Power Source* **112** 583

[13] Lindström R W, Seidel Y E, Jusys Z, Gustavsson M, Wickman B, Kasemo B and Behm R J 2010 *J. Electroanal. Chem.* **664** 90

[14] Niu Z Q, Ma W J, Dong H B, Li J Z and Zhou W Y 2011 *Chin. Phys.* B **20** 028101

[15] Xu J, Lee S H, Bell Zane W, Smith B, Zhang X G, Ju Tong, Chen A J and Pan Z W 2010 *Proc. SPIE Int. Soc. Opt. Eng.* **7805** 78050Z

[16] Machado M, Piquini P and Mota R 2005 *Nanotechnology* **16** 302