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Local electric field and configuration of CO molecules adsorbed on a nanostructured surface with nanocones*

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Based on the nanostructured surface model that the (platinum, Pt) nanocones grow out symmetrically from a plane substrate, the local electric field near the conical nanoparticle surface is computed and discussed. On the basis of these results, the adsorbed CO molecules are modelled as dipoles, and three kinds of interactions, i.e. interactions between dipoles and local electric field, between dipoles and dipoles, as well as between dipoles and nanostructured substrate, are taken into account. The spatial configuration of CO molecules adsorbed on the nanocone surface is then given by Monte-Carlo simulation. Our results show that the CO molecules adsorbed on the nanocone surface cause local agglomeration under the action of an external electric field, and this agglomeration becomes more compact with decreasing conical angle, which results in a stronger interaction among molecules. These results serve as a basis for explaining abnormal phenomena such as the abnormal infrared effect (AIRE), which was found when CO molecules were adsorbed on the nanostructured transition-metal surface.

Keywords: metallic nanostructured surface, nanocone, adsorbed molecules, local electric field
PACC: 7155, 7340, 3640

1. Introduction

The investigation of spectral absorption properties of metallic nanomaterials has been an active topic in recent years.[1−5] Special attention has been paid to the abnormal infrared effect (AIRE), which was found when CO molecules were adsorbed on a nanostructured transition-metal surface.[5,6] On the surfaces of some metals (e.g. platinum, rhodium), when the nanoparticles grow to a certain size, instead of a Gaussian-type spectral line shape, enhanced asymmetric line shapes of anti-absorption have been found,[6] some of which can be classified as Fano-like line shapes.[7,8] A similar enhanced anti-absorption (positive-going peak) with an increased band width was also detected for agglomerated nanoparticles. It has been found that the infrared adsorption is enhanced with further agglomeration of nanoparticles.[9] It is universally accepted that the formation mechanism of the AIRE is rather complicated and there is no mature theory for reference so far. Some reported results have shown that the infrared spectral line shape is determined by molecular polarizability.[10,11] However, molecular polarizability is related to the interactions between adsorbed molecules and local electric field, between adsorbed molecules and adsorbed molecules, as well as between adsorbed molecules and nanostructured metallic substrate.[11] In the present paper, both the nanostructured surface model and the mathematical model are proposed to study the local electric field near the nanocone surface, as well as the spatial configuration of the adsorbed molecules on the nanocone surface. It is believed that research into the AIRE mechanism is conducive to investigating the physical properties of nanostructured metallic surfaces.

2. Theoretical model

Consider an adsorption system composed of an array of conical nanoparticles in a two-dimensional hexagonal configuration grown out from a grounded metal plane. An external electric field (E_0) is applied in the normal direction with respect to the surface as shown in Fig.1. If the number of nanoparticles is large enough, it is reasonable to treat them in an identical

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manner (since all conical nanoparticles are electrically equivalent). For convenience, we consider a hexagonal close packing structure of nanoparticles on a two-dimensional plane, and 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.2.

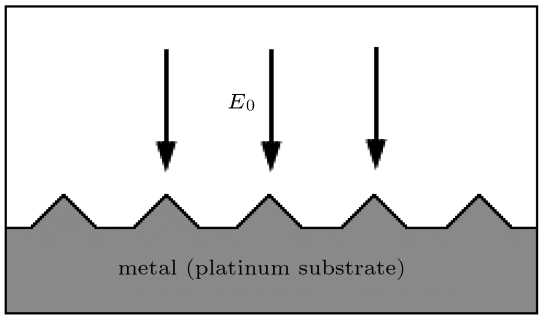


Fig.1. A metallic nanostructured surface with nanocones in the uniform electric field.

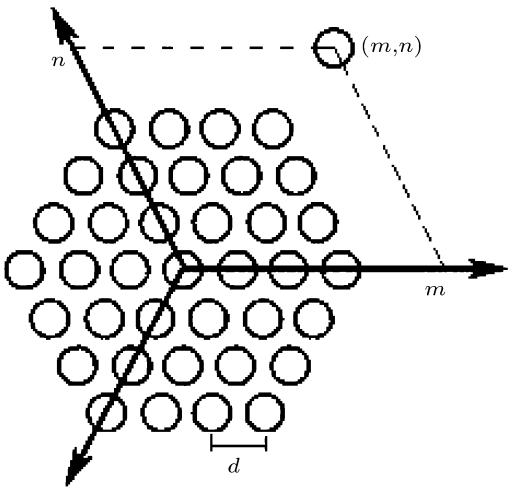


Fig.2. Hexagonal array of nanocones and the non-orthogonal $2\pi/3$ coordinate system.

2.1. Local electric field

Firstly, we investigate the distribution of the local electric field near the surface of a nanocone with a conical angle of 2α (see Fig.3). If we use the spherical coordinate system, the angular ranges of the free space are $0 \le \theta \le \beta$, $0 \le \phi \le 2\pi$, and $\beta = \pi - \alpha$. Therefore,

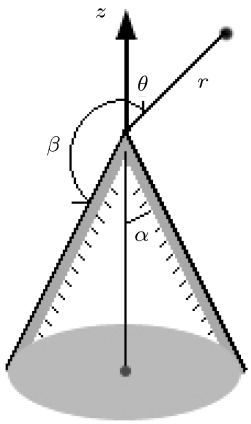


Fig.3. Nanocone and spherical coordinate system.

the proposed problem is a three-dimensional electrostatic problem with a symmetrical z-axis and a boundary condition of the grounded metal nanocone (the electric potential equals zero). Since the space symmetry is in electric field distribution, the electric potential can be expressed as

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

The electrostatic boundary condition is given by

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

Since expression (1) must satisfy Laplace's equation, we have

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

and Legendre's equation

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

where A and B are both undetermined constants, and $x = \cos\theta$. For any space point of the angular areas of interest of $\cos\beta \le x \le \cos 0°$, the unique solution of expression (1), or of expression (3) and Eq.(4) must satisfy the boundary condition of expression (2). When $x = \cos 0° = 1$, $P(x)$ must be a regular function. Therefore, the solution of Eq.(4) must be expanded into a power series solution for $x = 1$. In order to meet this requirement, we let $y = (1-x)/2$, then Eq.(4) becomes

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

where we have substituted λ for l in Eq.(4) and expression (3) due to the fact that the λ is no longer an integer as l. Now the power series solution of Eq.(5) is defined as

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

From Eq.(5) and expression (6), we have the recurrence relation for the coefficients as

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

Since the electric potential must be a finite value at the coordinate origin (i.e. $r = 0$), we have $B = 0$ in expression (3). From expression (1), the basic solution of the electric potential is given by

$$\Psi(r,\theta) = Ar^{\lambda}P_{\lambda}(x) = Ar^{\lambda}P_{\lambda}(\cos\theta). \tag{8}$$

According to the boundary condition of expression (2) and expression (8), we have

$$P_{\lambda}(\cos\beta) = 0. \tag{9}$$

For a given β, in general, there exists infinite λ satisfying Eq.(9), i.e. λ_i $(i = 1, 2, 3, \ldots)$ constitutes an eigenvalue sequence. When $\lambda = \lambda_i, \cos\beta$ is the ith zero point (or root) of Eq.(9). According to the linear superposition method, the final solution of the electric potential should be the linear superposition of the basic solution (expression (8)). However, we are concerned only with the characteristics of the electric field near the surface of the nanocones or the origin of the coordinate system (i.e. $r \to 0$, see Fig.3), and the electric field that exists far from the nanocone is not taken into account; therefore, only a few lower order items of the linear superposition of expression (8) can approximate to the solution of the local electric field. Furthermore, in view of the six-fold symmetry of the nanocone array, the linear superposition of the local electric field distribution should also be of six-fold symmetry. Then the approximate solution (expression (1)) can be expressed as

$$\begin{aligned}\Psi = {} & -E_0 r\cos\theta + a_1\sum_{m,n} r_{mn}^{\lambda_1}P_{\lambda_1}(\cos\theta_{mn}) \\ & + a_2\sum_{m,n} r_{mn}^{\lambda_2}P_{\lambda_2}(\cos\theta_{mn}) \\ & + a_3\sum_{m,n} r_{mn}^{\lambda_3}P_{\lambda_3}(\cos\theta_{mn}) \\ & + a_4\sum_{m,n} r_{mn}^{\lambda_4}P_{\lambda_4}(\cos\theta_{mn}) \\ & + a_5\sum_{m,n} r_{mn}^{\lambda_6}P_{\lambda_6}^{6}(\cos\theta_{mn})\cos(6\varphi_{mn}),\end{aligned} \tag{10}$$

where $P_{\lambda_6}^{6}(\cos\theta_{mn})$ denotes the non-integer-order associated Legendre functions, E_0 is the external field, r is the distance of the position of interest from the origin, and subscripts (m and n) represent the position of the nanoparticles; r_{mn}, θ_{mn}, and φ_{mn} denote the distance, the polar angle, and the azimuthal angle of the position of interest (m and n) respectively. They can be determined by spherical coordinates r, θ, ϕ and (m and n) from geometrical relations. The numerical coefficients $a_1 - a_5$ are determined by boundary conditions for the contributions of terms 2–6 on the right-hand side of expression (10) respectively. The associated Legendre functions are taken into account due to the six-fold symmetry of our non-orthogonal coordinate system. Now, the local electric field near the surface of the nanocones can be determined by

$$E_r = 0, \quad \text{and} \quad E_\theta = -\frac{\partial\Psi}{r\partial\theta}, \quad (\theta = \beta). \tag{11}$$

2.2. Interaction energy

Previous research has demonstrated that when CO molecules are adsorbed on a metallic nanoparticle surface, the C atom of CO always moves towards the nanoparticle, and the O atom then keeps away from the nanoparticle, so that each and every CO produces an equivalent dipole moment which interacts with other dipole moments as well as the local electric field. It is easy to analyse that each CO molecule with dipole moment μ will be agglomerated towards the top of the nanocones and oriented in a direction perpendicular to the nanocone surface due to its interaction with the local electric field, resulting in an interaction energy

$$W_1 = -\mu\sum_{i}^{N} E_i, \tag{12}$$

where N is the number of CO molecules adsorbed on one nanocone. Besides the dipole–electric field interaction, on nanocone surface CO molecules interact with each other through an equivalent dipole–dipole interaction, and the effect of dipole–dipole interaction will cause a repulsion between them. The dipole–dipole interaction energy is given by

$$W_2 = -\frac{\mu^2}{2}\sum_{i\neq j}^{N}\frac{3\,(\boldsymbol{e}_{ri}\cdot\boldsymbol{r}_{ij})(\boldsymbol{e}_{rj}\cdot\boldsymbol{r}_{ij}) - (\boldsymbol{e}_{ri}\cdot\boldsymbol{e}_{rj})r_{ij}^2}{4\pi\varepsilon_0 r_{ij}^5}, \tag{13}$$

where N is the average number of CO molecules adsorbed on each nanoparticle, $\boldsymbol{e}_{ri}$ is the unit vector in

the r-direction at position $\boldsymbol{r}$ on the nanoparticle surface and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $r_{ij} = |\boldsymbol{r}_{ij}|$. The interactions among dipoles attached to different nanoparticles are neglected due to the large distances between them. However, there still exists a significant interaction between adsorbed molecules and the atoms of metallic nanostructured substrate, which should be taken into account for the CO–Pt system in Ref.[12], and the CO–Pt interaction can be given by a Rose-like function as

$$W_3 = -\frac{1}{2}\sum_{i\neq j} E_0^{AM}[1 + b(r_{ij}]\mathrm{e}^{-b(r_{ij})} \qquad (14)$$

and

$$b(r_{ij}) = \alpha(\frac{r_{ij}}{r_0} - 1), \qquad (15)$$

where $E_0^{\mathrm{AM}} = 1.77$ eV, which is related to the energy of adsorption; $r_0 = 0.24$ nm, which is related to the distance of the C–Pt atom; $\alpha = 10.75$, which is related to the rigidity of adsorbed CO or the vibrational properties of CO–Pt bond. Therefore, under the interaction of the external electric field, the total interaction energy of the three kinds of interactions is $W = W_1 + W_2 + W_3$. It is apparent that the interaction energy among dipoles will become larger as the agglomeration of CO molecules becomes closer and closer to each other, and the internal electric field inside the molecule causes a change in the equivalent molecular polarizability: this change can produce the anti-absorption infrared effect.[11]

3. Results and discussion

In our calculations, a total of 1141 identical platinum nanocones in a two-dimensional hexagonal array are considered, which corresponds to $(m, n)_{\max} = (20, 20)$ in Fig.2. The bottom radius of a nanocone $R = 5$ nm (or 7.5 nm), the distance between two adjacent nanocones $d = 10.5$ nm (or 16 nm), and the number of CO molecules adsorbed on one nanocone $N = 6 \times 54 = 324$. The external field $E_0 = 6 \times 10^8$ V/m, which is estimated according to the typical spectra of CO adsorption and applied in the z-direction to the nanostructured Pt substrate. After the numerical coefficients $a_1 - a_5$ of expression (10) are determined by the boundary condition expression (2), the local electric field near the surface of a nanocone can be determined from expression (11). Figure 4 shows the distribution of local electric field on one nanocone surface, the range of cross section radii is chosen as 2.5–4.0 nm.

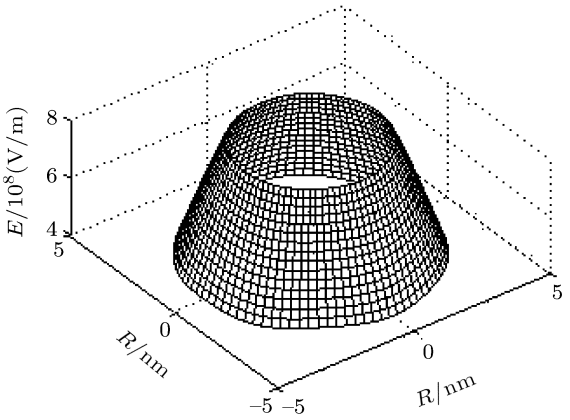


Fig.4. Distribution of local electric field on one nanocone surface.

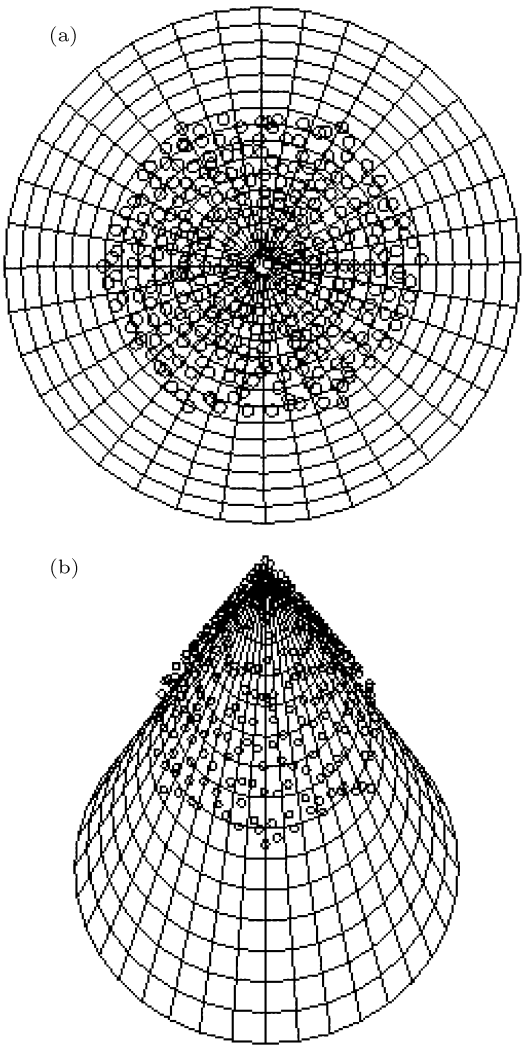


Fig.5. Spatial configuration of CO molecules adsorbed on a platinum nanocone.

In order to obtain the spatial configuration of CO molecules adsorbed on the platinum nanocone surface, off-lattice Monte Carlo simulations are carried

out according to the principle of the global minimum of the total interaction energy $W = W_1 + W_2 + W_3$ given by expressions (12)–(15). In our simulations, 3.24×10^6 iterations (equivalent to 10000 Monte Carlo steps (MCS)) are carried out, which demonstrates that a stable result is achieved without spending too much time on computation. The spatial configuration of CO molecules adsorbed on a platinum nanocone is shown as a top view of the coverage and a three-dimensional form in Figs.5(a) and 5(b).

Figures 5(a) and 5(b) show that a definite agglomeration of CO molecules tends to the top of the nanocone and a coverage is symmetrical and hexagonal due to the symmetrical array of nanocones.

4. Conclusion

In order to understand theoretically the formation mechanism of AIRE, the local electric field near the platinum nanocones is computed and discussed when an external electric field is applied to a nanostructured platinum substrate with nanocone arrays. Under the consideration of three kinds of interactions, i.e. interactions between adsorbed molecules and local electric field, between adsorbed molecules and adsorbed molecules, and between adsorbed molecules and nanostructured platinum substrate, the adsorbed CO molecules are modelled as dipoles, and the spatial configuration of CO molecules adsorbed on the nanocone surface is obtained by using Monte–Carlo simulation. Our computational results show that the agglomeration of adsorbed molecules becomes more compact with decreasing geometrical size (especially the conical angle) of nanocones, thereby leading to a more intensive interaction between molecules. This physical picture provides a reasonable basis for explaining the AIREs.

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