

THEORETICAL INVESTIGATION ON THE ADSORPTION AND DIFFUSION OF ATOMS/IONS ON THE SURFACE OF TWO-DIMENSIONAL NANOCRYSTAL

Li-Jun Zhou¹, Jian-Gang Guo² and Xin-Xin Yao²

¹ Department of Mechanical Engineering, Tianjin University of Technology and Education, Tianjin 300222, China, zhoulj_tj@163.com

² Tianjin Key Laboratory of Modern Engineering Mechanics, School of Mechanical Engineering, Tianjin University, Tianjin 300072, China, guojg@tju.edu.cn

Keywords: Atom/ion, Two-dimensional nanocrystal, Adsorption, Diffusion, Interaction potential

ABSTRACT

Theoretical investigations are made on adsorption and diffusion of atoms/ions on the surface of two-dimensional nanocrystal based on an analytical model. An atom/ion interacts with every atom of the two-dimensional nanocrystal through a pairwise potential which can be approximated by the Lennard-Jones (L-J) potential. Using the Fourier expansion of the interaction potential, the total interaction energy between the adsorption atom/ion and the two-dimensional nanocrystal is derived. Adsorption energy and adsorption stability of atoms/ions are analyzed on three special sites for three kinds of typical crystal surfaces.

1 INTRODUCTION

Two-dimensional nanocrystals have excellent mechanical, thermal and electrical properties, and they have potential applications in many fields. The adsorption and diffusion of atoms/ions on the surface of two-dimensional nanocrystal is significant in the fields of high sensitivity sensors, atomic-scale friction, rechargeable lithium-ion batteries, energy storage and drug delivery system (DDS) and so on, which has attracted much attention in recent years and some researches have been made [1-10]. However, there are still some unsolved scientific questions for its applications.

2 THEORETICAL MODEL

A two-dimensional nanocrystals with periodic lattice structure is assumed to be perfect, flat and infinite compared to atomic scale (as shown in Fig. 1).

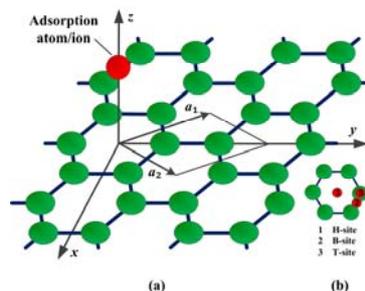


Figure 1. Schematics of (a) an adsorption atom/ion and a two-dimensional nanocrystal, (b) lattice structure with three particular adsorption sites: hollow (on top of a lattice, H-), top (on top of an atom, T-), and bridge (on top of a bond, B-).

An adsorption atom/ion is on top of two-dimensional nanocrystal. The interaction between the atom/ion and nanocrystal can be defined by van der Waals force. It is assumed that a 6-12 L-J potential is applied to determine the van der Waals interaction potential between the adsorption atom and each atom in the nanocrystal. What's more, due to the periodic surface lattice structure of

nanocrystal, the total interaction potential $u(\mathbf{r})$ between the adsorption atom and nanocrystal surface can be expressed via a Fourier series [7-8],

$$u(\mathbf{r}) \approx w_0(z) + \sum_{g>0} \sum_{k=1}^q w_g(z) \exp[i\mathbf{g} \cdot (\mathbf{m}_k + \boldsymbol{\tau})], \quad (1)$$

where,

$$w_0(z) = \frac{2\pi\varepsilon q}{A} \left(\frac{2\sigma^{*12}}{5z^{*10}} - \frac{\sigma^{*6}}{z^{*4}} \right) \text{ and } w_g(z) = \frac{2\pi\varepsilon}{A} \left[\frac{\sigma^{*12}}{30} \left(\frac{g}{2z} \right)^5 K_5(gz) - 2\sigma^6 \left(\frac{g}{2z} \right)^2 K_2(gz) \right], \quad (2)$$

where q is the number of the nanocrystal atoms in the unit cell and A the area of unit cell (as shown in Figure 1), ε and σ denote the potential well depth and the distance when the interaction potential is equal to zero, respectively, K_2 and K_5 are the modified Bessel function of the second kind, and g is dependent on the surface lattice structure of nanocrystal.

For nanocrystals with hexagonal, square and triangular lattice, the dimensionless total interaction potential between the adsorption atom/ion and the nanocrystal can be derived in the Cartesian coordinate system as shown in Figure 1, respectively,

$$u^*(r) = \lambda q \left(\frac{2\sigma^{*12}}{5z^{*10}} - \frac{\sigma^{*6}}{z^{*4}} \right) - \lambda(\alpha - \beta) \cdot \left[2 \cos\left(\frac{2\pi}{\sqrt{3}} y^*\right) \cos(2\pi x^*) + \cos\left(\frac{4\pi}{\sqrt{3}} y^*\right) \right], \quad (3)$$

$$u^*(r) = \lambda q \left(\frac{2\sigma^{*12}}{5z^{*10}} - \frac{\sigma^{*6}}{z^{*4}} \right) - \lambda(\alpha - \beta) \cdot \left[\cos(2\pi x^*) + \cos(2\pi y^*) \right], \quad (4)$$

$$u^*(r) = \lambda q \left(\frac{2\sigma^{*12}}{5z^{*10}} - \frac{\sigma^{*6}}{z^{*4}} \right) + \lambda(\alpha - \beta) \cdot \left[2 \cos\left(\frac{2\pi}{\sqrt{3}} x^*\right) \cos(2\pi y^*) + \cos\left(\frac{4\pi}{\sqrt{3}} x^*\right) \right], \quad (5)$$

where dimensionless parameters have following forms, $A^* = A/a^2$, $z^* = z/a$, $g^* = ga$, $\sigma^* = \sigma/a$, $x^* = x/a$, $y^* = y/a$, $u^* = u/\varepsilon$, $\lambda = 2\pi/A^*$, $\beta = 2\sigma^{*6} (g^*/2z^*)^2 K_2(g^*z^*)$, $\alpha = \sigma^{*12} (g^*/2z^*)^5 K_5(g^*z^*)/30$.

3 RESULTS AND DISCUSSIONS

The Eqs. (3)-(5) describe the interaction potentials between a single adsorption atom/ion and the nanocrystal surface with different lattice structure (hexagonal, square and triangular lattice), respectively. For the convenience of discussion, three typical two-dimensional nanocrystals (graphene, caesium chloride (CsCl) and molybdenum disulfide (MoS₂)) are selected. Their lattice structures are hexagonal, square and triangular, respectively. It can be found from the Eqs. (3)-(5) that the values of the interaction potential are dependent on the position of the adsorption atom/ion on crystal surface and the parameters of L-J potential which is varied for different nanocrystal. A hydrogen atom (H atom) is chosen as the adsorption atom. The L-J potential parameters can be specified for H atom and the surface atoms of three typical two-dimensional nanocrystals. Then the interaction potentials between the H atom and two-dimensional nanocrystals can be calculated via the Eqs. (3)-(5) when it is at the different positions of crystal surface.

The variations of interaction potential between the H atom and three two-dimensional nanocrystals are illustrated in the Figure 2 and 3 with respect to the positions in the x , y and z directions, respectively. It can be seen from Figure 2 that the potential curves are periodic in the x and y directions, and there are three periodic equilibrium positions, corresponding to three particular adsorption sites of H atom on crystal surface. They are hollow (on top of a lattice, H-), top (on top of an atom, T-), and bridge (on top of a bond, B-) sites (as shown in Figure 1(b)), respectively. At three adsorption sites, the equilibrium height and interaction potential at the equilibrium which can be called binding energy are different. Moreover, via the equilibrium equations in the z direction, the equilibrium height and binding energy at three adsorption sites can be calculated for three kinds of nanocrystals, respectively. For different nanocrystals, the equilibrium height and binding energy at the each adsorption site are different. However, for three nanocrystals, the equilibrium height and binding energy at the H-site are the lowest, followed by those at the B-site, and those at the T-site are the

highest. Thus, H-site is the most stable adsorption site, and T-site is the most unstable. Figure 3 shows the variations of interaction potential of the H atom at the T-sites of three nanocrystals along the z direction. Although the variation trends are almost identical for the three nanocrystals, the equilibrium height and binding energy are also different.

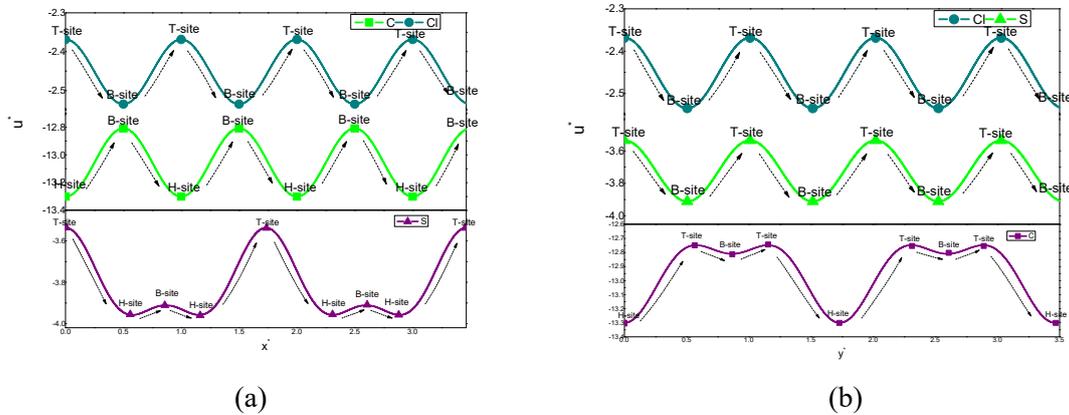


Figure 2. The variations of interaction potential between H atom and three kinds of nanocrystals in the (a) x-direction and (b) y-direction, respectively

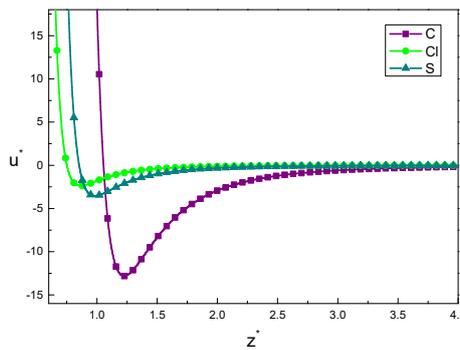


Figure 3. The variations of interaction potential of H atom and three kinds of nanocrystals at T-site along the z-direction

Since the binding energy of an adsorption atom/ion at three adsorption sites is different, the atom/ion has to get over an energy barrier when it migrates from an adsorption site to another one. The energy to drive the atom/ion is defined as diffusion energy. Obviously, the diffusion energy is dependent on the two-dimensional nanocrystal itself. As shown in the Figure 2, the energy barriers are different for different nanocrystal, different surface lattice structure and different diffusion path when the H atom diffuses along x or y direction on the surface of nanocrystal.

4 CONCLUSIONS

An analytical model is presented to investigate the interaction potential when an atom/ion is adsorbed and diffuses on the surface of two-dimensional nanocrystals, the mechanism of adsorption and diffusion are discussed. The equilibrium height and binding energy at three particular adsorption sites are illustrated and analyzed for three kinds of typical nanocrystals, and the adsorption stability are discussed. The order from low to high for both equilibrium height and binding energy is H-site, B-site and T-site, and H-site is the most stable adsorption site. When an adsorption atom/ion diffuses on the surface of nanocrystal, there are energy barriers it has to get over, which are dependent on the nanocrystal, its surface lattice structure and diffusion path.

ACKNOWLEDGEMENTS

The work is supported by the National Natural Science Foundation of China (Grant no. 11372216 and 11502167) and the Development Fund of Tianjin University of Technology and Education (Grant no. KJ14-52).

REFERENCES

- [1] M. Amft, S. Lebegue, O. Eriksson and N.V. Skorodumova, Adsorption of Cu, Ag, and Au atoms on graphene including van der Waals interactions, *J. Phys.: Condens. Matter*, **23**, 2011, pp. 395001.
- [2] T.L. Chan and J.R. Chelikowsky, Controlling diffusion of lithium in silicon nanostructures, *Amer. Chem. Soc.*, **10**, 2010, pp. 821-825.
- [3] L. Xian and M.Y. Chou, Diffusion of Si and C atoms on and between graphene layers, *J. Phys. D: Appl. Phys.*, **45**, 2012, pp. 455309.
- [4] Y. Xia, Z. Li and H.J. Kreuzer, Adsorption, diffusion and desorption of hydrogen on graphene, *Surf. Sci.*, **605**, 2011, pp. 70-73.
- [5] H. Tachikawa, A direct molecular orbital-molecular dynamics study on the diffusion of the Li ion on a fluorinated graphene surface, *J. Phys. Chem. C*, 2008, 112: 10193-10199.
- [6] H. Tachikawa, T. Iyama and H. Kawabata, MD simulation of the interaction of magnesium with graphene, *Thin Solid Films*, **518**, 2009, pp. 877-879.
- [7] Y.Z. Yu, J.G. Guo and L.J. Zhou, Theoretical investigation on the adsorption and diffusion of lithium-ion on and between graphene layers with size and defect effects, *Adsorpt. Sci. Technol.*, **34**, 2016, pp. 212-226.
- [8] Y.Z. Yu, J.G. Guo and Y.L. Kang, An analytical model for adsorption and diffusion of atoms/ions on graphene surface, *J. Nanomater.*, **2015**, 2015, pp. 382474.
- [9] M. Chi and Y.P. Zhao, Adsorption of formaldehyde molecule on the intrinsic and Al-doped graphene: A first principle study, *Comp. Mater. Sci.*, **46**, 2009, pp. 1085-1090.
- [10] C. Uthaisar and V. Barone, Edge effects on the characteristics of Li diffusion in graphene, *Nano Lett.*, **10**, 2010, pp. 2838-2842.