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The theoretical studies on the adsorption and migration of hydrogen atom on the two-dimensional nanocrystal surface

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Abstract. An analytical model is presented to study the adsorption and migration of atoms/ions on the surface of two-dimensional nanocrystal. 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 a hydrogen atom are analyzed on three special sites for three kinds of typical crystal surfaces. The interaction potential of the hydrogen atom migrating along specific paths on the surface of three kinds of typical nanocrystals is illustrated and analyzed.

1. Introduction

Two-dimensional nanocrystals have excellent mechanical, thermal and electrical properties, and they have potential applications in many fields. The adsorption and migration 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.

Amft *et al.* [1] made a systematic density functional study (DFT) on the adsorption of Cu, Ag and Au adatoms on pristine graphene. According to the differences of the total energies at the three adsorption sites, they found that the migration of Cu and Au took place along carbon-carbon bonds, while the Ag adatoms could move almost unrestrictedly on graphene sheet. By the same methods, Xian *et al.* [2] studied the potential energy variations and migrations of Si and C atoms on a single layer of graphene and between graphene sheets, and they found that Si atoms could move almost freely on graphene and between graphene layers, while C atoms had much larger migration barriers. Ji *et al.* [3] investigated the adsorption of lithium atom on graphene, and three different adsorption sites were taken into consideration. They found that the hollow site was found to be the most stable, followed by the bridge and top sites. What's more, Xia *et al.* [4] studied the adsorption, migration and desorption of hydrogen on the graphene surface by DFT method.

Apart from DFT method, Zhou *et al.* [5] studied the adsorption and migration of lithium on the graphene with divacancy and Stone-Wales defects using the first-principles calculations to understand the effect of point defects on the lithium adsorption on graphene, and the results showed that the presence of point defects could enhance the lithium adsorption on graphene. Tachikawa *et al.* [6]



studied the migration processes of the lithium-ion on a fluorinated graphene surface by means of a direct molecular orbital-molecular dynamics (MO-MD) method. The interaction of Mg atom with graphene was also researched by using MD simulations [7]. Uthaisar *et al.* [8] studied the influence of edge effects of graphene on the migration of lithium-ion on the graphene surface. Yu *et al.* [9, 10] made a theoretical investigation on adsorption and migration of atoms/ions on graphene surface based on an analytical continuous model, and they also discussed the influence of edge and size effects of graphene on the migration of atoms/ions.

In this work, a theoretical model will be presented to investigate the adsorption stabilities of atoms/ions on the surface of two-dimensional nanocrystal, and the total interaction energy between the adsorption atom/ion and two-dimensional nanocrystal will be derived. Moreover, adsorption energy and adsorption stability of a hydrogen atom will be analyzed on three special sites for three kinds of typical crystal surfaces. The interaction potential of a hydrogen atom moving along specific paths on the surface of three kinds of typical nanocrystals is illustrated and discussed.

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).

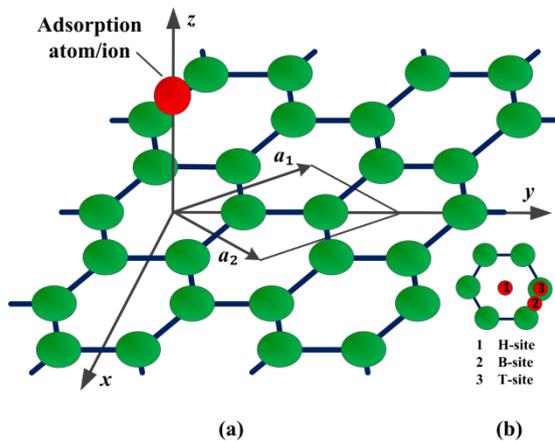


Figure 1. Schematics of (a) an adsorption atom/ion and a two-dimensional nanocrystal, (b) lattice structure with three particular adsorption sites: hollow (on top of a lattice, H-), top (on top of an atom, T-), and bridge (on top of a bond, B-).

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 $u(r)$ between the adsorption atom and nanocrystal surface can be expressed via a Fourier series [9, 10].

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

where,

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

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.

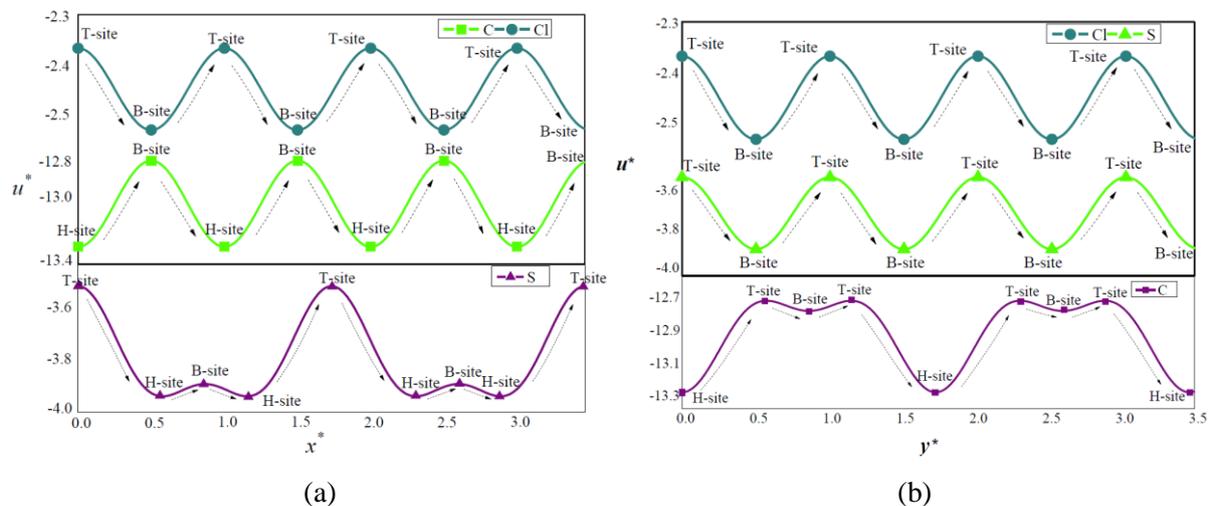


Figure 2. The variations of interaction potential between H atom and three kinds of nanocrystals in the (a) x-direction and (b) y-direction, respectively.

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.

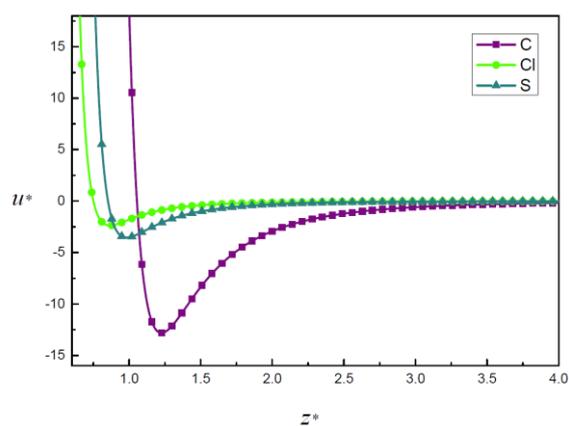


Figure 3. The variations of interaction potential of H atom and three kinds of nanocrystals at T-site along the z -direction

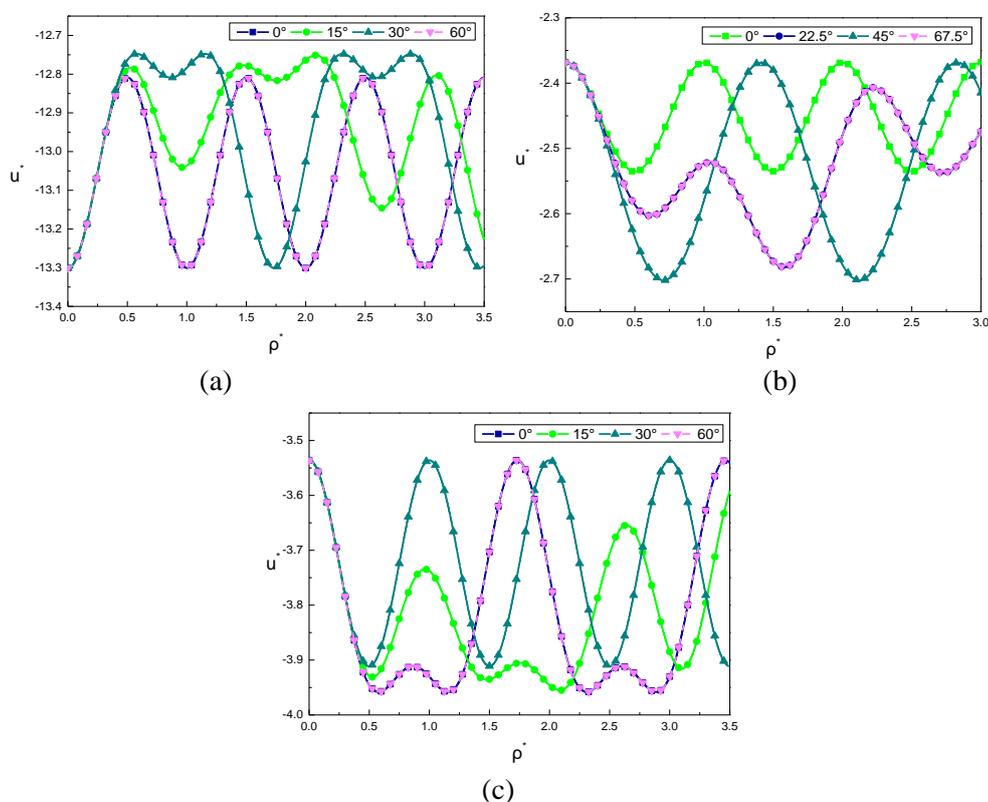


Figure 4. The dimensionless interaction potential is path-dependent and the path-dependence is periodic when a hydrogen atom migrates (a) along 0° , 15° , 30° , 60° angles from the x -axis on the graphene surface, (b) along 0° , 22.5° , 45° , 67.5° angles from the x -axis on the CsCl surface, (c) along 0° , 15° , 30° , 60° angles from the x -axis on the MoS_2 surface.

Since the binding energy of the H atom at three adsorption sites is different, the H atom has to get over an energy barrier when it migrates from an adsorption site to another one. The energy to drive the H atom is defined as migration energy. Obviously, the migration energy is dependent on the migration path. It is assumed that a hydrogen atom migrates along the specified paths, and its initial adsorption site is assumed to be H-site. The dimensionless interaction potentials between the H atom and three kinds of nanocrystals for different migration directions are illustrated in the Figure 4. It can be found from these figures that the periods of interaction potential are varied for different migration directions, and the minimum migration energy are also varied., i.e., the migration of the H atom on nanocrystal surface is path-dependent. What's more, the path-dependence exhibits periodic. It can be found along the same lattice orientation, such as 0° and 60° angles for graphene, the variations of interaction potential are same.

4. Conclusion

An analytical model is presented to investigate the interaction potential when an atom/ion is adsorbed and migrates on the surface of two-dimensional nanocrystals, the mechanism of adsorption and migration 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 migrates on the surface of nanocrystal, there are energy barriers it has to get over, and the migration is path-dependent, and the path-dependence exhibits periodic.

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