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MoS_2 decoration by Mo-atoms and MoS_2-Mo-graphene heterostructure: A theoretical study

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Here we proposed a completely new covalent heterostructure based on graphene and self-decorated MoS_2 monolayer. Detailed investigation of decoration process of the MoS_2 surface by Mo adatoms was performed using *first principles DFT* methods. Comparison between valence-only and semicore pseudopotentials was performed to correctly describe the interaction between Mo adatoms and MoS_2 surface. It was found that self-decoration by Mo atoms is favorable from energetic point of view. We studied in detail various decoration paths of Mo atoms on the MoS_2 surface. The strong variation of electronic properties after the decoration of MoS_2 was found. The impact of the presence of Mo adatoms to the electronic properties of graphene/MoS_2 heterostructure was shown.

Introduction

The developing field of two-dimensional materials reached the stage of investigation of complex nanostructures based on already known 2D films. The available experimental data hold promise for establishing a completely new scientific field of artificial quasi-two-dimensional heterostructures with properties dependent on constituted 2D layers.[1-4] This perspective attracts significant attention to the investigation of the surface of the 2D nanostructures, especially to their interaction with additional atoms which is highly important for the creation of an atomically sharp interface between neighbored films in the heterostructure. The surface properties of transition metal dichalcogenides are most important because atomic films of such composition are usually part of a new generation of 2D heterostructures due to their semiconducting properties and chemical robustness.[5] Nevertheless the additional atom~~s~~ adsorption can lead to a substantial changing of the film properties. For example, the adsorption of Li atoms on MoS_2 or WS_2 can lead to the transition of the semiconducting 2H phase to the metallic 1T phase.[6-9] Partial transformation and coexistence of two phases by structural stabilization through substitutional doping[10] or adsorption of metal atoms on the TMD's surface[11] may be a valuable way to achieve metal-semiconductor hybrid structures.

Moreover Lin et al[12] demonstrated the doping (deposition) with Re and Au atoms on single layer MoS_2 using a Chemical Vapor Transport (CVT) technique and also it was shown experimentally in consistence with DFT calculations that adsorbed Re enhance the local chemical affinity, evidenced by agglomeration of other dopant/impurity atoms. Motivated by these results we suggest here the formation of layered heterostructures connected with each other by adsorbed metal atoms. From the wide variety of possible metals we have chosen molybdenum itself in terms of homoadsorption. Molybdenum can for example be deposited on MoS_2 in an atomic layer deposition (ALD) process.[13]

Intermediate metal links could change the interaction inside the heterostructure from Van der Waals to covalent, tune the electronic properties and increase the mechanical characteristics associated with shear deformations.

Results and discussion

Here we focused on the investigation of interaction between graphene and the MoS_2 surface through Mo adatoms which were adsorbed directly on the MoS_2 surface. Surprisingly we discovered that despite of the inertness of the MoS_2 surface the decoration process of Mo adatoms is energetically favorable, whereas the small value of the estimated migration barrier hints on a high mobility of Mo atoms on the surface. This result allows the conclusion that the MoS_2 surface can be decorated by individual Mo adatoms which can substantially change the electronic and chemical properties of the layer. Finally, we investigated the properties of double-layer heterostructure graphene/MoS_2 with Mo atoms attached to the MoS_2 surface and found out that the adatoms may form bonds between layers and introduce new states near Fermi energy which may create conduction channels.

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All calculations in the paper are based on first-principal calculations within density functional theory (DFT) with the projected augmented waves method (PAW) implemented in VASP package [14,15] using periodic boundary conditions within a supercell geometry. General gradient approximation of the Perdew-Burke-Ernzerhof [16] parameterization was applied. The plane wave cutoff and Brillouin zone sampling were determined after test calculations. To avoid the interaction between periodic images the large spacing ~10 Å was used in nonperiodic directions – perpendicular to the layer. Cutoff energy for plane wave basis set was set to be 400 eV. To calculate equilibrium atomic structures, the Brillouin zone was sampled according to the Monkhorst-Pack scheme with a 6×6×1 k-point set for a 4×4 supercell of MoS_2. Structural relaxation was performed until the forces acting on each atom became less than 0.05 eV $Å^{-1}$.

Valence-only pseudopotential ($4d^5 5s^1$) and semicore pseudopotential ($4p^6 4d^5 5s^1$) for Mo atoms were used for description of interaction between adatom and MoS_2 surface. Both GGA and LDA approaches taking into account spin polarization were applied for test calculations. The formation energy of MoS_2 layer and the binding energy of Mo adatom were calculated using both types of pseudopotentials. The formation energy per MoS_2 unit was calculated by

$$E_f = E_{tot} - mE_{Mo} - nE_S ,$$

where E_{tot}, E_{Mo}, E_S are the total energies of the MoS_2 unit cell, of the ground state of isolated Mo and isolated S atoms, respectively. The total energies of isolated atoms were obtained using the same unit box as in the case of 4×4 MoS_2 supercell calculation. The formation energy of the MoS_2 layer was obtained as -22.32 eV/MoS_2 and -22.07 eV/MoS_2 for LDA and -16.33 eV/MoS_2 and -14.53 eV/MoS_2 for GGA with valence-only and semicore pseudopotentials, respectively. The difference between the formation energy values is caused only by the ground state energy of the isolated Mo atom. The total energy of the ground state calculated with GGA in the case of semicore pseudopotentials is 1.5 eV lower than that in the case of a valence-only one. LDA underestimates the ground state energy of isolated Mo atom and overestimates the formation energy, respectively. The binding energy of Mo adatoms depends also on the type of the Mo pseudopotential. All further calculations were carried out with the GGA semicore pseudopotential due to the good agreement of the formation energy with reference data. [17]

Calculations of partial density of states of heterostructures based on graphene and decorated MoS_2 were carried out with a localized orbitals method implemented in the SIESTA package. [18] The exchange-correlation energy was approximated by the LDA. [19] The plane-wave mesh cutoff was defined as 250 Ry. The band structures were calculated along Γ-M-K-Γ directions using 50 k-points in each direction.

We studied in detail the decoration process of the MoS_2 surface by Mo adatoms (self-decoration). Two possible binding sites of Mo adatoms on the MoS_2 surface were considered. These sites are defined by the different positions of the Mo adatoms with respect to the atoms in the layer, depicted in Figure 1a, namely as S-1 and S-3. The decoration process of individual Mo atoms was studied on the surface of the 4×4 MoS_2 supercell.

The binding energy as function of the decoration was calculated as:

$$E_b = E_{tot} - E_{MoS_2} - E_{atom}$$

where E_{tot}, E_{Mo}, E_S are the total energies of the MoS_2 layer with an additional Mo atom, a pure MoS_2 layer and energy of an isolated Mo atom, respectively. The binding energy between the Mo adatom and the MoS_2 surface was determined as -1.23 eV and -1.51 eV for S-1 and S-3 sites, respectively. The energetically favorable location of a Mo atom at a S-3 site (on top of a Mo atom in the layer) allows us to consider ~~for~~ the further study only for this site. The decoration process was performed atom by atom onto the surface of the supercell in two paths: asymmetric path, when adatoms firstly cover the upper side and then the lower side of the surface (blue numbers in Figure 1b) and a symmetric path in which adatoms placed alternately on both surfaces (red numbers in Figure 1b). The distance between the adatoms was chosen to be more than 4 Å to avoid the interaction between neighboring adatoms on the surface. In Figure 1b the comparison between the binding energies per Mo adatom for both paths of decoration are presented. We found out that the energetically preferred decoration is the asymmetric one - when adatoms firstly cover one side of the film and chemically activate the other side for binding. In this case the binding energy monotonically increases in absolute value with the increasing number of Mo adatoms. In case of the symmetric path (red color) the increase of the number of adatoms leads to a step-like increasing (in absolute value) of the binding energy whereas.

After the uniform coverage of both MoS_2 surfaces both paths yield the same binding energy (eighth step at Figure 1c). Further adsorption of the Mo adatom on the MoS_2 surface leads to the formation of Mo_2 clusters on the surface (see inset of Figure 1c). During this process the binding energy strongly decreases down to -1.94 eV, which is possible due to the reconstruction of the surface and formation of the Mo clusters by increase of the distance between Mo_2 and MoS_2 up to ~2.8 Å.

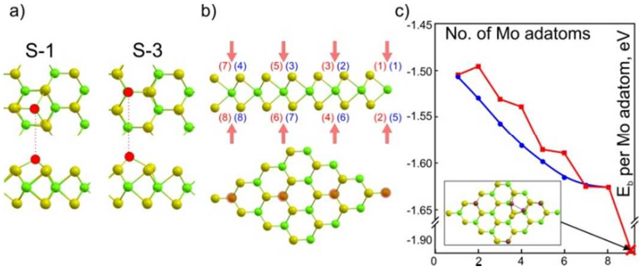

Figure 1 (a) atomic structure of MoS_2 with Mo adatoms in S-1 and S-3 sites. (b) Schematic representation of symmetric and asymmetric decoration paths (red and blue numbers correspond to the sequence of adsorption in symmetric and asymmetric paths, respectively). (c) Dependence of the binding energy per Mo adatom on the number of Mo adatoms on the surface. Red circles depicted Mo adatoms onto MoS_2 surface. In the inset the atomic structure of MoS_2 surface with 9th Mo adatoms in supercell is shown. By dark red circles the Mo adatoms depicted.

The possible formation of Mo_2 dimers requires an analysis of the migration barrier of adatoms on the MoS_2 surface. The migration from S-1 to S-3 sites was studied (Figure 2). It was found that the energy barrier from S-3 site (energy favorable) to S-1 site is ~0.48 eV per unit cell, whereas the reverse energy barrier from S-1 to S-3 is only 0.20 eV per unit cell, which could possibly be overcome at room temperature.

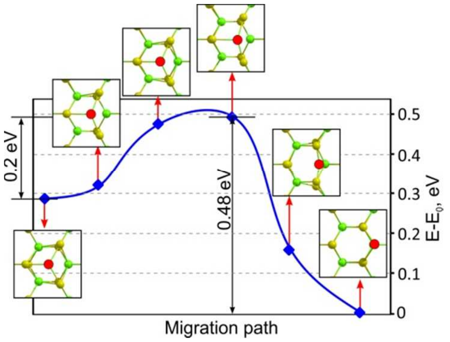

Figure 2 The migration barrier of Mo adatoms on MoS2 surface from S-1 to S-3 site. By red circles the adatoms were depicted.

Taking into account the low migration barriers it is possible to conclude that a MoS_2 surface can be covered only by scarcely distributed Mo adatoms without cluster formation. Besides of changing in binding energy Mo adatoms strongly impact on the electronic properties of the MoS_2 surface. The evolution of electronic properties at each step of decoration was investigated (Figure 3). Adsorption of even the first Mo adatom (Figure 3) leads to a strong decrease of the band gap (from 1.8 eV to 0.8 eV) with formation of several additional impurity levels in the valence band.

In Figure 4 the electronic densities of states for all steps of decoration are shown. Red and blue colors correspond to the symmetric and asymmetric decoration paths, respectively. In the inset of Figure 4 the decoration paths are sketched. Further decoration leads to the increase of the contribution of impurity levels in the valence band and a slow decrease of the band gap. After the adsorption of a 5th Mo adatom only a small difference between the symmetric and asymmetric paths is observed. Finally at the maximal number of Mo adatoms (8 atoms) the band gap is decreased down to 0.4 eV from 1.6 eV (pure MoS_2) layer.

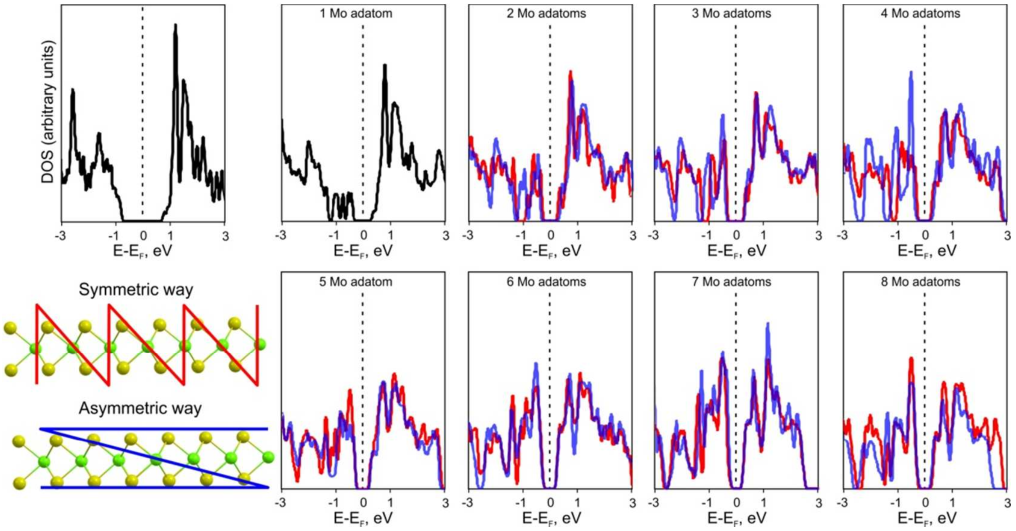

Figure 3 Evolution of electronic properties of MoS2 supercell decorated by 1-8 Mo adatoms. Schematic representation of the type of decoration path shown on the left. Red and blue colors correspond to the symmetric and asymmetric decoration paths, respectively

After the detailed study of the decoration process onto a MoS_2 surface and the impact on electronic properties the investigation of layered structure based on graphene and decorated MoS_2 (covalent heterostructure) was carried out. We considered a hexagonal supercell consisting of (4×4) MoS_2 and (5×5) graphene unit cells with Mo adatom between the layer. In Figure 4 the detailed analysis of electronic properties of a covalent heterostructure is presented. Mo adatoms formed covalent bonds with a graphene surface as well as with a MoS_2 surface which strongly changes the electronic structure (Figure 4b).

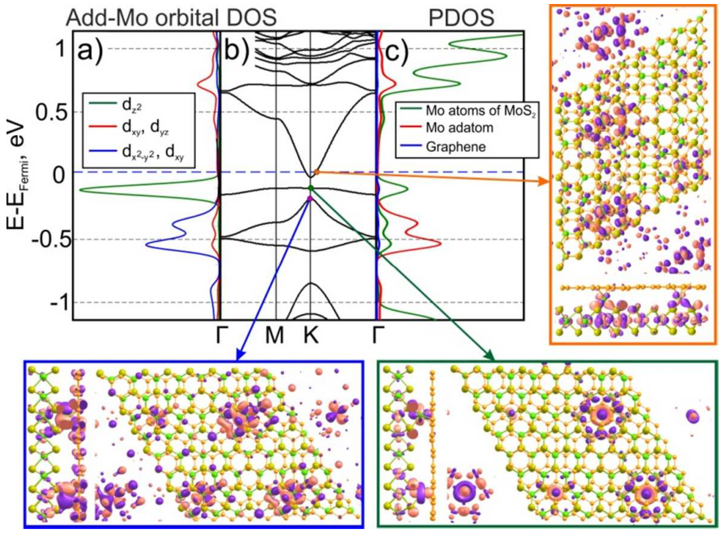

Figure 4 (a) Orbital DOS of covalent heterostructure based on graphene and decorated MoS_2 layers; (b) Band structure; (c) Partial DOS of covalent heterostructure. By Green, red and blue colors PDOS of Mo atoms in the layer, Mo adatom and graphene, respectively. Insets illustrate the wave function at energy levels indicated by circles in the band structure diagram.

The Mo adatoms play the role of a connecting link between graphene and MoS_2. Partial DOS for *d* orbitals of an additional Mo atom in the heterostructure, band structure and partial DOS for the heterostructure with Mo atoms between the layers are presented in Figure 4. To estimate the contribution from each type of orbital of additional Mo atoms between the layers of MoS_2 and graphene the wave function of selected energy levels are shown also in Figure 4. The Mo atoms between the layers introduce the new states with the energy close to the E_F (Figure 4b). Detailed analysis of PDOS of the considered heterostructure show that the $d_z{}^2$ orbitals of additional Mo atoms are responsible for the connection between the graphene and MoS_2 surface (green line in Figure 4a). Moreover $d_z{}^2$ orbitals play a major role in a formation of a link between the layers in the heterostructure.

Conclusions

A detailed theoretical study of the decoration process of the MoS_2 surface by Mo adatoms was performed. Comparison between the energies of two possible binding sites displays different behavior upon the adatoms concentration. We found that self-decoration is preferred from the energetic point of view. Two various decoration paths named as symmetric and asymmetric were studied. Strong increase of binding energy during the decoration was observed for both decoration types. The strong variation of electronic properties after the decoration of MoS_2 was observed. The impact of the presence of Mo adatoms to the graphene/MoS_2 heterostructure electronic properties was also shown. It was found that the presence of Mo adatoms between the layers increases the interaction and conductive channels between graphene and MoS_2 are formed.

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1 R. V. Gorbachev, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. Tudorovskiy, I. V. Grigorieva, A. H. MacDonald, S. V. Morozov, K. Watanabe, T. Taniguchi *et al.*, *Nature Physics,* 2012, **8,** 896.
2 S. J. Haigh, A. Gholinia, R. Jalil, S. Romani, L. Britnell, D. C. Elias, K. S. Novoselov, L. A. Ponomarenko, A. K. Geim, R. Gorbachev *et al.*, *Nat Mater,* 2012, **11,** 764.
3 L. A. Ponomarenko, A. K. Geim, A. A. Zhukov, R. Jalil, S. V. Morozov, K. S. Novoselov, I. V. Grigorieva, E. H. Hill, V. V. Cheianov, V. I. Fal'ko *et al.*, *Nature Physics,* 2011, **7,** 958.
4 F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A. P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, A. I. Tartakovskii *et al.*, *Nat Mater,* 2015, **14,** 301.
5 M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, H. Zhang, *Nature Chemistry,* 2013, **5,** 263.
6 J. A. Wilson, A. D. Yoffe, *Advances in Physics,* 1969, **18,** 193.
7 R. F. Frindt, A. D. Yoffe, *Proc. R. Soc. Lond. A,* 1963, **273,** 69.
8 R. Bissessur, M. G. Kanatzidis, J. L. Schindler, C. R. Kannewurf, *Journal of the Chemical Society, Chemical Communications,* 1993, 1582.
9 M. A. Py, R. R. Haering, *Canadian Journal of Physics,* 1983, **61,** 76.
10 T. Lorenz, D. Teich, J. O. Joswig, G. Seifert, *J. Phys. Chem. C,* 2012, **116,** 11714.
11 Y. C. Lin, D. O. Dumcenco, Y. S. Huang, K. Suenaga, *Nature Nanotech.,* 2014, **9,** 391.
12 Y. C. Lin, D. O. Dumcenco, H. P. Komsa, Y. Niimi, A. V. Krasheninnikov, Y. S. Huang, K. Suenaga, *Advanced Materials,* 2014, **26,** 2857.
13 D. Seghete, G. B. Rayner Jr, A. S. Cavanagh, V. R. Anderson, S. M. George, *Chem. Mater.,* 2011, **23,** 1668.
14 G. Kresse, J. Furthmüller, *Computational Materials Science,* 1996, **6,** 15.
15 G. Kresse, J. Furthmüller, *Phys. Rev. B,* 1996, **54,** 11169−11186.
16 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77,** 3865.
17 A. R. Botello-Méndez, F. López-Urías, M. Terrones, H. Terrones, *Nanotechnology,* 2009, **20,** 325703.
18 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *Journal of Physics: Condensed Matter,* 2002, **14,** 2745.
19 J. P. Perdew, A. Zunger, *Phys. Rev. B,* 1981, **23,** 5048.