ARTICLE IN PRESS

Chemical Physics Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

The prospect of sensitizing organic dyes attached to the MoS_2 surface: Physical insights from density functional theory investigations

Hung M. Le [a,b,*], Viet Q. Bui [c], Phuong Hoang Tran [d], Nguyen-Nguyen Pham-Tran [d], Yoshiyuki Kawazoe [e], Duc Nguyen-Manh [f]

[a] Computational Chemistry Research Group, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[b] Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[c] Department of Applied Chemistry and Institute of Natural Sciences, Kyung Hee University, Gyeonggi-do 446-701, South Korea
[d] Faculty of Chemistry, University of Science, Vietnam National University, Ho Chi Minh City, Viet Nam
[e] New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan
[f] Theory and Modeling Department, Culham Centre for Fusion Energy, United Kingdom Atomic Energy Authority, Abingdon OX14 3DB, United Kingdom

ARTICLE INFO

Article history:
Received 26 September 2016
In final form 4 November 2016
Available online xxxx

Keywords:
Organic dye
MoS_2
DFT

ABSTRACT

In this theoretical study, we employ first-principles calculations to explore the bonding nature of organic dyes on the semiconducting MoS_2 surface. To achieve good bonding interaction and charge transfer, the —COO. residue needs to form ionic bonds with the defected MoS_2 surface. In the cases of L0 and a newly synthesized dye named as TN1, we observe the manifestation of an in-gap state at -1 eV from the Fermi level, which might enhance photon trapping capability of the complex.

1. Introduction

Molybdenum disulfide, a two-dimensional (2D) material with multi-layer stacking of MoS_2, has been known to possess applications in several aspects. In industry, this material is well-known as a lubricant because of the weak van der Waals' interactions between layers, which thereby produces a low friction coefficient [1]. Interestingly enough, such weak van der Waals interactions have a significant influence on the electronic property of MoS_2 and its close derivative in the family, WS_2. Adopting angle-resolved photoelectron spectroscopy and first-principles calculations, Klein et al. [2] showed that in the multi-layer form, the material would possess an indirect band gap of around 1.2 eV, while the standalone single layer establishes a larger direct band gap of $\sim$1.8 eV. Besides, its novel catalytic capability also guarantees the wide applications of MoS_2 as a participating catalyst in hydrodesulfurization for petroleum refinery [3,4] and water splitting for hydrogen production [5]. In fact, for a period of time, MoS_2 had been considered as an inert material. This traditional belief is no longer true until the successful synthesis of highly-reactive anionic $[Mo_3S_{13}]^{2-}$ nanoparticles [6].

The single layer form of MoS_2 finally finds its position in electronics due to the successful synthesis of highly qualitative mono-crystalline layers [7]. Not only integrated into functional electronic devices, such a material with a direct band-gap can be employed in phototransistors with high sensitivity and low noise [8]. The functionalization of the MoS_2 layer have attracted much attention from the research community because of its promising applications in electronics, energy storage, sensing, and catalysis [9]. The covalent functionalization of MoS_2 was previously discussed by Presolski and Pumera [10]. Recently, Chen et al. [11] demonstrated a functionalization of exfoliated 2H-MoS_2 with cysteine, an organic thiol, and the results showed physisorption rather than covalent attachment. Using a first-principles approach, Ataca and Ciraci proposed the attachment of adatom and vacancy creation, which consequently caused MoS_2 to gain a net magnetic moment [12]. Due to the difficulty of functionalizing pristine MoS_2, a new strategy was proposed to attach the acetate group on the surface by employing transition metal bridges [13]. In the storyline of photo-sensitivity, there have been two remarkable efforts to tailor the performance of MoS_2 in photocatalysis [5] and photodetector [14]. In those studies, organic structures, being employed as 'sensitizing dyes' and possessing compatible photosensitivity with the heterogeneous layer, are employed to decorate the surface of MoS_2, and dedicate an essential role in 'trapping' photoexcitations. In the content of this study, we demonstrate a

---

* Corresponding author.
E-mail address: leminhhung@tdt.edu.vn (H.M. Le).

http://dx.doi.org/10.1016/j.cplett.2016.11.007
0009-2614/© 2016 Published by Elsevier B.V.

Please cite this article in press as: H.M. Le et al., Chem. Phys. Lett. (2016), http://dx.doi.org/10.1016/j.cplett.2016.11.007

theoretical investigation of organic dye attached to an MoS_2 surface to get more insights of the binding nature and in-gap occupations. The organic dyes of interest consist of the well-known L0 structures [15,16] and one in-house-factorized dye. However, prior to investigating the interactions between a large organic molecule and MoS_2 surface, it is necessary to get deeper understanding how a basic carboxylic residue, i.e. formic acid (HCOOH), could establish attachment to MoS_2.

2. Computational details

First-principles calculations based on density functional theory (DFT) are employed as the main investigating method in this study. The Perdew-Bucke-Ernzerhof (PBE) functional [17–19] implemented in the Vienna Ab Initio Simulation Package (VASP) [20–22] is utilized and the projector-augmented wave method [23] is employed to construct electronic wave-functions for the participating atoms. Grimme's D3 empirical corrections for long-range van der Waals' interactions are activated for all investigated models [24]. For the assumption of lattice circulation in the x and y directions, a (5 × 5) super-cell of MoS_2 consisting of 75 atoms are employed with the c-axis length chosen as 28 Å to guarantee surface isolation. For computational feasibility, the constant volume optimization scheme is executed with a force convergence criterion of 10^{-4} eV. The cut-off energy level of 400 eV and a k-point mesh of (3 × 3 × 1) are chosen.

3. Results and discussion

3.1. Attachment of HCOOH/HCOO$^\cdot$ on the pure/defected MoS_2 surface

The basis of binding between a heterogeneous surface and organic dye structures relies on the terminated carboxylate residue, in which oxygen atoms can be attached to the surface [25]. Before going into the discussion with dye attachments, we first explore the physics and chemistry understanding of binding origin between an MoS_2 surface and the simplest carboxylic residue, HCOOH. In the first case, we assume there is neither surface defect nor formic acid reduction, i.e. the original structure of formic acid (HCOOH) is in direct contact with MoS_2. Because of surface inertness, only van der Waals interaction is formed to keep formic acid quite immobilized. By looking at the charge density cloud in Fig. 1(a), we observe that the H and O atoms seem to establish weak interactions with those S atoms on the surface. Quantitatively, to justify the statement of stability, we examine binding energy using the following equation:

$$E_{binding} = E_{surface} + E_{residue} - E_{complex} \quad (1)$$

where $E_{surface}$, $E_{residue}$, $E_{complex}$ denote the total energies of the MoS_2 surface (with S defect or without S defect depending on case study), organic ligand, and the whole binding complex, respectively. In Eq. (1), the magnitude of positive $E_{binding}$ indicates how strongly the residue is stabilized on the MoS_2 surface. As in the very first case, the binding energy is only 0.02 eV, which can be regarded as a very weak physisorption. In two previous studies [26,27], the physisorption of H_2O on the MoS_2/WS_2 monolayer was shown to be very weak and caused no adjustments on the electronic properties of the 2D layer. The eigenstates representing an HCOOH orbital show up as a non-bonding state, and the electronic structure of the thin film layer remains unaltered. Upon analyzing charge distribution (Fig. 1(a)), we observe insignificant charge transfer between MoS_2 and formic acid.

In the second case, we alternatively consider the attachment of the radical formate residue (HCOO$^\cdot$). There is a clear improvement on binding stability (i.e. binding energy is elevated up to 0.53 eV). In this case (Fig. 1(b)), both O atoms seem to reside on the surface and enhance van der Waals interactions with the most nearby S

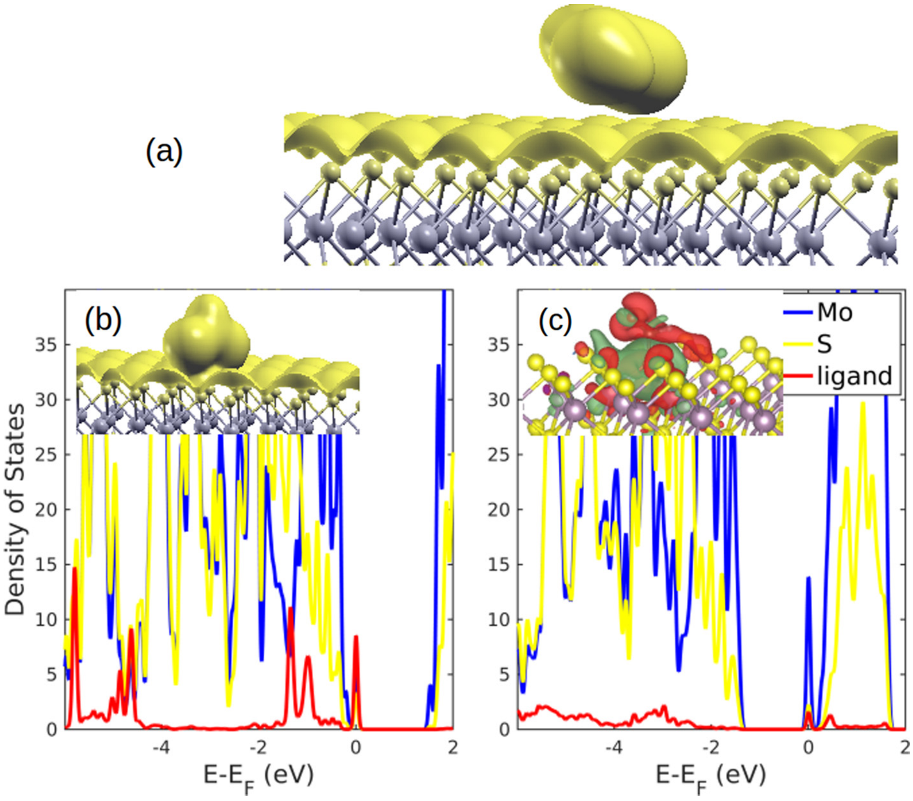

Fig. 1. (a) Charge density distribution of HCOOH interacting with the pure MoS2 monolayer, (b) partial DOS of HCOO$^\cdot$ absorption on MoS_2, and (c) partial DOS of HCOO$^\cdot$ absorption on $MoS_{2-\varepsilon}$.

Please cite this article in press as: H.M. Le et al., Chem. Phys. Lett. (2016), http://dx.doi.org/10.1016/j.cplett.2016.11.007