

Understanding Role of Precursor (Crystal Violet) and its Polarity on MoS₂ Growth; A First Principles Study

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Transition metal dichalcogenides (TMDs) such as MoS₂ is the thinnest semiconductor, exhibits promising prospects in the applications of optoelectronics, catalysis and hydrogen storage devices. Uniform and high quality MoS₂ is highly desirable in large area for its applications on commercial scale and fundamental research. Many experimental techniques i.e CVD have been developed to successfully synthesis MoS₂ on large scale, here in this work atomistic detail to understand the growth mechanism is addressed which was greatly overlooked. Here based on first principles calculation we found that polarity of seeding promoter (crystal violet considered in this work) controls the growth mechanism. It is also found that molybdenum destroys the precursor while sulfur adsorption with precursor is favorable.

INTRODUCTION

Transition metal dichalcogenides (TMD), MX₂ (M=Mo, W; X=S, Se, Te), have attracted considerable attention for their great potential in the fields of catalysis, nanotribology, microelectronics, lithium batteries, hydrogen storage, medical and optoelectronics. MoS₂ nano-materials have been known in the form of nested fullerene-like nanodots and one-dimensional nanotubes^[1]. Substantial efforts have been devoted to prepare thin-layer MoS₂, including scotch tape based micromechanical exfoliation, and intercalation assisted exfoliation, liquid exfoliation, physical vapor deposition, hydrothermal synthesis, thermolysis of single precursor containing Mo and S. The lateral size of the MoS₂ films synthesized by the aforementioned methods is often in the order of several micrometer; however, the synthesis of large-size MoS₂ thin layers is still a challenge.

Chemical vapor deposition (CVD) has been one of the most practical methods for synthesizing large-area graphene and graphene analogues such as boron nitride and BCN nanosheets. The sulfurization of MoO₃ using the CVD method has been adopted to synthesize MoS₂ materials; however, the reaction normally leads to

MoS₂ nanoparticles or nanorod structures during the synthesis. However, Xi Ling et al.,^[2] has reported that single and multilayers of MoS₂ can be synthesis by using seeding.

Crystal violet (CV) is one the potential candidate to synthesis uniform MoS₂ layer. Using LCAO-DFT lab first we found the energetically most stable structure of crystal violet. We also calculated the sulfur and molybdenum binding with precursor to observe the growth initiation of MoS₂ and we found growth will always start by sulfurization first.

I. CALCULATION METHODS

We applied a first-principles computational methods based on density-functional theory (DFT) for the electronic structure calculations. DFT calculations were carried out by adopting Perdew-Burke-Ernzerhof parameterization of generalized gradient approximation^[3] as exchange-correlation functional, using LCAODFT lab provided by EDISON_Nano. Core electrons were removed by adopting Troullier-Martins-type norm-conserving nonlocal pseudopotentials^[4], and Kohn-Sham pseudo-orbitals were expended in terms of double- ζ -plus-polarization numerical atomic

basis sets defined by the confinement energy of 80 meV. Real-space integration was performed with a mesh cut-off energy of 300 Ry. A $1 \times 1 \times 1$ Monkhorst-Pack \bar{k} -points sampling was employed for the integration of Brillouin zone. The ground state geometries were obtained by minimizing the forces on all the atoms until the forces converged to 0.02 eV/Å.

The precursor used in this work, tris(4-(dimethylamino)phenyl)methylm cation chloride also called crystal violet (CV), is comprised of two parts: metrhghyrosanilide (CV base) and chloride (Cl⁻). Each periodic image of CV molecule is sperated by a vaccme of 20Å to avoid artificial interaction between molecule and its periodic image. The charge distribution in CV molecule after chlorine adsorption is calculated based on Mulliken charge analysis provided in advanced option in LCAO-DFT lab. Jmol visualtizing tool was used to examine the structures and calculating tilte angle.

II. RESULTS AND DISCUSSION

According to the position of chloride with respect to CV base, we considered three different models of CV as shown in Figure 1. The maximum dihedral angle between the lower two benzene rings (ϕ) is 33.8°, 34.9° and 38.6° for models A, B and C, respectively. While the ϕ of CV molecule without Cl is 33.7° that is close to model A, which clarifies chlorine atom produce negligible distortion in CV base in model A and CV molecule retain its D3 symmetry. The adsorption energy of Cl atom on CV molecule (ΔE_{ads}) s calculated as

$$\Delta E_{ads} = E_{CV} - E_{base} - E_{Cl} \quad (1)$$

where ΔE_{ads} , E_{CV} , E_{base} and E_{Cl} is total energy of CV molecule, CV base, and chlorine atom, respectively.

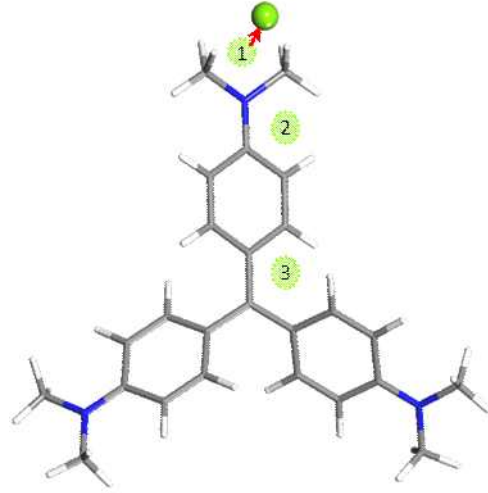


Figure 1. Crystal Violet (precursor) optimised structure and table 1, 2 and 3 corresponds to 3 possible initial position of chlorine considered in this work.

Model A is energetically favorable among the three models, being consistent with both experimental and theoretical values^[5,6]. The calculated adsorption energies of chlorine on CV base are presented in Table 1.

Table 1. Adsorption energies of chlorine with crystal violet molecule

Model	Adsorption Energy (eV)
1	-2.41
2	-2.30
3	-2.33

A. Sulfur adsorption on CV

In order to examine the sulfur binding to CV molecule, sulfur atom was allowed to bind on different sites of CV molecule. The adsorption energy of sulfur on CV (ΔE_{ads}) is evaluated as

$$\Delta E_{ads} = E_{(CV+S)} - E_{CV} - E_S \quad (2)$$

where ΔE_{ads} , E_{CV+S} , E_{CV} and E_S is total energy of CV with sulfur atom, CV, and sulfur atom, respectively.

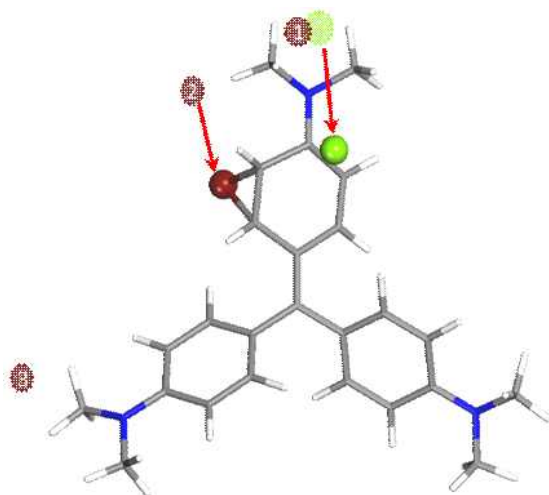


Figure 2. Sulfur adsorption on CV molecule (most stable structure), table 1, 2 and 3 corresponds to possible adsorption sites on CV molecule.

We considered three different models based on sulfur adsorption sites, as presented in Figure 2. Table 2 corresponds with scenario when sulfur atom adsorb on CV molecule while Cl atom is below the CV base. Rest of the two tables (1 & 3) analogous to the situation when S atom try to adsorb on polar and non-polar end of CV molecule shown as model III respectively. Green and dark red dim dotted circles (Figure. 2) represent the initial position of Cl and S atoms respectively before optimization. We found that the scenario when chlorine was initially at position labeled as 1 is energetically most stable one, moreover during sulfur binding chlorine atom moves towards the adsorption site (Figure. 2). The binding strength of each model is tabulated in Table 2.

Table 2. Calculated adsorption energies of sulfur atom with crystal violet molecule.

Model	Adsorption Energy (eV)
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1	-6.97
2	-6.54
3	-6.04

B. Molybdenum adsorption on CV

We also checked the possibility where molybdenum binds first to CV molecule. Although the binding energy is pretty large, molybdenum destroys the CV molecule in all the cases as shown in Figure 3 and Figure 4 where Mo adsorb on polar and non-polar part of crystal violet respectively. This validates the experimental observation where growth mechanism starts with sulfur binding first.

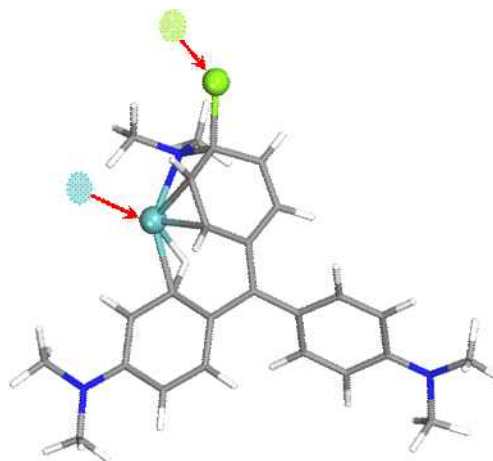


Figure 3. Mo adsorption on polar part of crystal violet molecule.

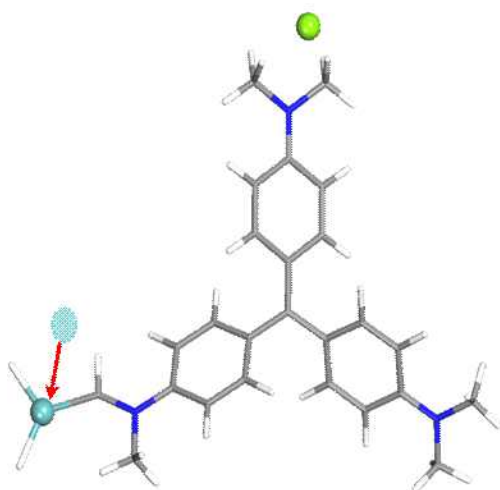


Figure 4. Mo adsorption on non-polar part of crystal violet molecule.

Here we concluded, growth will start be sulfur adsorption as precursor stability and symmetry is broken if Mo adsorb on crystal violet as shown in figure 3 and figure 4. Calculated binding energies of molybdenum to polar and non-polar end of CV are given in Table 3.

Table 3. Molybdenum adsorption on polar and non-polar end of crystal violet molecule.

Model	Adsorption Energy (eV)
polar	-9.56
non-polar	-6.11

In our ongoing work we are examining sulphur adsorption on crystal violet molecule on SiO₂ substrate to consider the substrate effect on sulfur binding with precursor.

III. CONCLUSION

DFT-based calculations have been performed to investigate the growth mechanism of MoS₂. Our results show that molybdenum adsorption destroys the precursor while sulfur adsorption is most favorable as crystal violet retain its stability and symmetry. In the case when chlorine is on the opposite side of crystal

violet base, sulfur atom strongly adsorbs on precursor and will initiate the uniform growth by providing strong adsorption bases.

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