Degradation of Cd-yellow Paints: ab initio study of the adsorption of oxygen and water on \{10.0\} CdS surface

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Abstract. The cadmium yellow paints (CdS) used in impressionist and modernist paintings in early 1900s are undergoing several deterioration processes, including whitening and discoloration. A relevant effect produced at the surface of the paintings is the growth of discolored crusts, formed mainly by white globular hydrated cadmium sulfate (CdSO$_4$·nH$_2$O) and cadmium carbonate (CdCO$_3$). Recent studies ascribe to an initial photo-oxidation process of CdS the input for the formation of such whitish compounds. In order to understand, at atomic level, the oxidation and hydration mechanisms of these whitish globules, we present the early stages of a theoretical study of the interaction between the hexagonal \{10.0\} surface of CdS and O$_2$ and H$_2$O molecules to simulate the combined effects of exposure to air and humidity. For this purpose, we adopted a first principles method within the framework of the Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA-PBE) with the use of ultrasoft pseudopotentials.

1. Introduction
Among the inorganic pigments, cadmium sulfide has high tinting, covering power, wide applicability, high stability in oil and water, pure hues ranging from very light yellow to orange, red and deep maroon-red. The cadmium pigments are meant to be cadmium sulfide crystallized in a hexagonal wurtzite lattice [1]. Cadmium sulfide with yellow color and high tinting forms the basis for all cadmium pigments. Consequently, important 19th to 20th century artists such as Claude Monet, Vincent Van Gogh, and Pablo Picasso frequently employed CdS in their paintings. Even though the cadmium sulfides are generally regarded as stable, various cases of specific deterioration noted on paintings have indicated that not all varieties are permanent. The deterioration occurs primarily in the lighter yellows, and involves discoloration (fading or whitening and a darkening) and loss of adhesion within the paint itself, producing chalking and crumbly surfaces. Phenomenons of deterioration are most pronounced in zones of thick impasto, while loss of the discolored uppermost layers reveals the light yellow below. The most showy feature of this degradation was the presence of whitish, semitransparent globules that were observed on top of the yellow paint. Cadmium carbonate (CdCO$_3$), cadmium oxide hydroxide,
cadmium carbonate oxide, and cadmium sulfate (CdSO₄) are potential CdS photodegradation products identified in the paintings [2]. In view of the fact that the pigment, cadmium sulfide, was historically synthesized by means of dry and wet processes and that CdCO₃ and CdSO₄ are reagents for this procedure, their identification alone does not constitute conclusive proof of photo-oxidation. This induced the researchers to propose a mechanism where, recurring cycles of moistening and drying could have eventually led to local accumulation of white globules CdSO₄·2H₂O at the paint surface after evaporation of the water. This type of degradation was found on the surface of faded cadmium yellow paints in the works of James Ensor (1860-1949) [3] and Henri Matisse[4, 5].

The goal of the current research is to understand the oxidation and hydration mechanisms of these whitish globules in the paint surface by means of Density Functional Theory within the generalized gradient approximation (DFT-GGA). To this end the \{10.0\} surface of CdS was considered as a preliminary benchmark. It was simulated according to the slab geometry and was next covered by oxygen, water molecules and a combination of O₂+ H₂O. More specifically, we determined the favorite adsorption sites and calculated the adsorption energies of the different molecules on top of the surface. The details of the electronic structure of the interactions are given via the bonding charge analysis along with a thorough description of the geometry.

2. Method

All the calculations are performed within the framework of the Density Functional Theory in the Generalized Gradient Approximation (DFT-GGA) as implemented in the quantum-ESPRESSO [6] suite of codes. Ultrasoft pseudopotentials (PBE) are used and van der Waals dispersion forces are accounted for. The Kohn-Sham equations were solved by using a plane waves basis set and the kinetic energy cutoffs for the electron wavefunctions and for the augmented electron density are 28 Ry and 280 Ry, respectively. The Brillouin zone sampling is performed with 4 × 4 × 4 and 4 × 4 × 1 k-points meshes for the bulk and surface structures, respectively. Valence electron configurations included Cd 5s² 5p² 4d¹⁰, S 3s² 3p⁴, O 2s² 2p⁴, and H 1s¹ states.

The surface energy for the cleavage surface is obtained from:

$$\gamma = \frac{E_{\text{sub}} - E_{\text{bulk}}}{2A}$$

Where \(E_{\text{sub}}\) is the total energy of the surface, \(E_{\text{bulk}}\) represents the total energy of a bulk structure - with the same symmetry - containing as many CdS-pairs as those in the surface, and A is the surface Area. The adsorption energy (\(E_{\text{ad}}\), always regarded as a measure of the strength of adsorbate-substrate adsorption, is defined as follows:

$$E_{\text{ad}} = E_{\text{sub}+\text{mol}} - [E_{\text{sub}} + nE_{\text{mol}}]$$

In which \(E_{\text{sub}+\text{mol}}\) is the total energy of the combined system containing the surface and n molecules, \(E_{\text{sub}}\) is the total energy of the clean surface, and \(E_{\text{mol}}\) is the energy of a single isolated molecule. The bonding charge analysis, that gives an estimate of the electron charge transfer, was evaluated according to the scheme proposed in Ref.[7], using the following expressions:

$$\Delta \rho(\mathbf{r}) = \rho_{\text{sub}+\text{mol}}(\mathbf{r}) - \rho_{\text{sub}}(\mathbf{r}) - \rho_{\text{mol}}(\mathbf{r})$$

Where \(\rho_{\text{sub}+\text{mol}}(\mathbf{r})\), \(\rho_{\text{sub}}(\mathbf{r})\) and \(\rho_{\text{mol}}(\mathbf{r})\) are the charge densities of the whole system, the isolated substrate and the adsorbate, respectively.
3. Results and Discussion

The CdS \{10.0\} surface was cleaved on the basis of the optimised hexagonal (wurtzite) structure along the direction perpendicular to the [1010]. The computed lattice parameters for the bulk were \(a=4.13\,\text{Å}, \ c=6.72\,\text{Å}, \ c/a=1.62\) which resulted in very good agreement, within the 0.5%, with the experimental values: \(a_{\text{exp}}=4.14\,\text{Å}, \ c_{\text{exp}}=6.72\,\text{Å}, \ (c/a)_{\text{exp}}=1.62\) [8]. A slab containing 5 atomic layers was sufficient to represent the CdS \{10.0\} surface since increasing the number of layers up to 7 layers both the surface energy and the interatomic distances showed no remarkable changes. Due to periodic boundary conditions, the slabs were separated by 20 Å of vacuum to avoid interaction between images.

All the atoms were allowed to relax. The structure of the relaxed CdS \{10.0\} surface showed a characteristic ridged profile: the under-coordinated Cd cations relaxed inward, toward the bulk, whereas the under-coordinated S anions relaxed outward. (see Figure 1). The positions of the atoms in outermost layer are defined in terms of lateral distances \(D\) in either \(x\) or \(y\) directions parallel to the surface and interlayer distances perpendicular to the surface \(\perp\).

Figure 1. Side view of the ideal (left) and relaxed (right) configuration of the CdS \{10.0\} surface. Distances \(D_{1,4x}\) and \(D_{1,4\perp}\) are meant to be the distances between the atom 1 and the atom 4 along the \(x\) direction and the \(z\) direction, respectively. The complete set of calculated values is given in Table 1 in comparison with the results of Barnard and collaborators [9].

In Table 1 are summarised the results of the interatomic distances obtained for the ideal and relaxed clean surface in comparison with the results of Barnard et al. [9] obtained with a similar DFT-GGA approach. Also in this case the agreement is excellent, within 1.0% for all the distances but the \(D_{1,2\perp}\) that turns out to be 0.02 Å shorter than that obtained in Ref. [9]. The discrepancy might be attributed to the difference in the size of the simulation cell. In Ref. [9] the periodic surface has a \(2 \times 2\) symmetry versus the \(2 \times 1\) of our work.

The calculated surface energy turns out to be \(\gamma = 0.28\,\text{Jm}^{-2}\), which is identical to that obtained in Ref. [9] To simulate the combined effects of exposure to air and humidity, the CdS \{10.0\} surface was allowed to interact with isolated oxygen, water and then with a combination of \(\text{O}_2+\text{H}_2\text{O}\). For this specific case, the molecules and the three outermost atomic layers of the surface were allowed to relax, while the two bottom layers were kept fixed to the bulk positions to simulate the infinite crystal. As for the isolated \(\text{O}_2\) molecule, four setups were considered as initial conditions, where the molecules were differently placed on top of the surface sites prior the relaxation. More specifically, the molecules were initially positioned at a distance as large as 2 Å above the Cd and S sites in both the two non-equivalent positions, namely the on-top and hollow ones, respectively. In Figure 2, the lowest energy relaxed configuration with \(\text{O}_2\) located on top the Cd ion is shown. This position corresponds to an adsorption energy as large as -12.99 kJmol\(^{-2}\) indicating the molecule to be physisorbed. In this case both the intra- and interlayer distances did not change remarkably while the O-O bond within the oxygen molecule increases from 1.20 Å to 1.23 Å. The bonding charge analysis reveals an accumulation of charge in the region between \(\text{O}_2\) and the Cd surface ion (red area) indicating a rearrangement of electron charge around the \(\text{O}_2\) molecule. The oxygen molecule was then replaced by a water molecule.
Table 1. Interatomic distances

|       | CdS ideal | relaxed | Barnard et al. [9] |
|-------|-----------|---------|-------------------|
| D_{1,2}x | 2.53      | 2.29    | 2.29              |
| D_{1,3}x | 0.84      | 0.64    | 0.65              |
| D_{1,4}x | 3.37      | 3.50    | 3.50              |
| D_{1,2}y | 0.00      | 0.00    | 0.00              |
| D_{1,3}y | 2.09      | 2.07    | 2.07              |
| D_{1,4}y | 2.09      | 2.06    | 2.07              |
| D_{1,2}⊥ | 0.00      | 0.80    | 0.78              |
| D_{1,3}⊥ | 1.20      | 1.30    | 1.31              |
| D_{1,4}⊥ | 1.21      | 1.55    | 1.57              |

Figure 2. Interaction between the CdS \{10.0\} surface and an isolated O_2 molecule: relevant interatomic distances (left) and bonding charge analysis (right)

The result is shown in Figure 3. The H_2O moved toward the hollow-Cd. The adsorption energy, $E_{ad} = -32.09 \text{ kJmol}^{-1}$, is higher than that obtained for O_2 and yet, the mechanism suggested is again a physisorption. Also in this system, no evident displacements of the atoms in the substrate are detected. The change of the angle within the water molecule is, conversely, noticeable. It appears to decrease from 104.39° to 103.25°, with are close, within 1%, to the experimental value 104.5° [10].

Concerning the bonding charge analysis, the water dipole was evident and a slight accumulation (red area) of the charge between oxygen and the surface hollow-Cd resulted in opposition to a depletion of charge (blu area) in the hydrogen regions. Finally, a combination of O_2 and H_2O was observed.

Figure 3. Interaction between the CdS \{10.0\} surface and an isolated H_2O molecule: relevant interatomic distances (left) and bonding charge analysis (right)
H$_2$O was considered. The two molecules were placed on the surface and let free to relax. The final configuration is reported in Figure 4. The O$_2$ molecule holds the favorite adsorption site above the on-top Cd while H$_2$O is located on top of the hollow-S and is oriented parallel to the surface with the oxygen atom closer to O$_2$. Again, no atomic position changed within the substrate. The angle H$\hat{O}$H decreases from 104.39° to 103.25°. A re-arrangement of the charge results in an accumulation in the region between H$_2$O and S and partially between O$_2$ and Cd. The adsorption energy of this system, $E_{ads} = -46.40$ kJmol$^{-1}$, indicates a physisorption.

The present work has to be regarded as a preliminary study of the combination of elemental molecules interacting with CdS. Further calculations considering different initial conditions and concentrations are in progress.

4. Conclusion
The structure and electronic properties of CdS \{10.0\} surface were studied using a fully theoretical model within the DFT-GGA framework. The adsorption of oxygen and water isolated molecules along with a combination of them was considered. The physical adsorption of the aforementioned molecules on the cleavage surface turns out to be the dominant mechanism. Further investigation considering a defective surface and/or surfaces of different symmetry are to be taken into account.

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