Reactivity of Cd-yellow pigments: Role of surface defects

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\textbf{A B S T R A C T}

The cadmium yellow paints used in several paintings of the early 1900s are undergoing a process of deterioration the reasons of which are still unclear. Structural defects in CdS, among other possible causes like photo-oxidative reactions, may play a role in the degradation process. Their presence in the pigment surface enhances the reactivity of cadmium sulfide. We present a theoretical study of the interaction between the hexagonal defective \((10\overline{10})\) surface of CdS and \(O_2\) and \(H_2O\) molecules to simulate the combined effects of exposure to air and humidity. The geometrical and electronic structures as well as the adsorption energies are determined with the use of a first principles method. All the calculations are performed within the framework of the Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA-PBE) with the use of ultrasoft pseudopotentials. The nudged elastic band method (NEB) is also considered to evaluate activation barriers and minimum reaction paths in two case studies, namely the dissociation of a water molecule in the presence of a cadmium vacancy and the uptake of one oxygen molecule by the CdS surface containing a sulfur vacancy. This paper highlights the key role that theoretical modelling can play in the application of materials science to art conservation.

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1. Introduction

A severe and irreversible alteration process is taking place in both historic mineral-based pigments and modern synthetic pigments used in painting as a consequence of their interaction with external agents present in the environment and with light. The strong yellow colouration of cadmium sulfide aroused great interest of artists soon after it was discovered. In spite of its excellent reputation with regards to permanency, the degradation of cadmium yellow occurs primarily in the lighter yellows, and involves discoloration (fading and darkening) producing chalky and crumbly surfaces. This alteration was ascribed to an initial photo-oxidation of CdS. For a long time, the complex alteration of cadmium sulfide was studied [1–7]. Indeed, this compound was known to suffer from degradation under the influence of sunlight and humidity. Despite the fact that this phenomenon is rather ambiguous and does not take place systematically, recent hypothesis has been given to explain the discoloration process. A gradual fading of originally bright yellow areas, painted with the pigment cadmium yellow paints, is observed in the following works: \textit{Still Life with Cabbage} [2] by James Ensor, \textit{The Joy of Life} [3,4] and \textit{Flower Piece} [5] by Henri Matisse.

The degradation mechanisms behind these alterations are often complex, involving traces of synthesis starting reagents or other impurities in the paint, requiring the presence of multiple degradation agents. In this theoretical work, form first principles, the degradation process of cadmium yellow pigments is linked to the interaction between the defective CdS surface and oxygen and water molecules. Theoretical modelling plays an important role in the field of conservation of works of art. With powerful predicting features, it is complementary to the experimental investigation and is of great support in the interpretation of results. In particular, we focus on the interaction between Cd- and S- vacancies in the most stable CdS surface, namely the \((10\overline{10})\), and oxygen/water molecules in the attempt to contribute preliminarily to the debate on the photo-oxidation mechanisms experimentally invoked [2,5,7] to interpret the appearance of the whitish globules in the paint surface. To this end the \((10\overline{10})\) surface of CdS was simulated according to the slab geometry and was next covered by oxygen, water molecules and a combination of \(O_2\) and \(H_2O\). 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 at the interface are given via density of states and bonding charge analysis along with a thorough description of the geometry.

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2. Theoretical method

All the calculations presented were performed within the framework of the Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA-PBE) as implemented in the quantum-ESPRESSO [8] package, with the use of ultrasoft pseudopotentials [9,10]. The dispersion corrected (DFT-D2) approach [11,12] was used to add the van der Waals (vdW) dispersion forces to the interactions between molecules and CdS. Hexagonal lattice parameters calculated including the dispersion correction \((a_0 = 4.20 \text{ Å} \text{ and } c = 6.95 \text{ Å})\) were slightly overestimated (within 3\%) with respect to the experimental values \((a_{\text{exp}} = 4.14 \text{ Å} \text{ and } c_{\text{exp}} = 6.71 \text{ Å})\), as expected in GGA approximation. The starting geometry of the surface was cleaved on the basis of the optimised hexagonal (wurtzite) structure along the direction perpendicular to the [1010]. The Brillouin zone sampling was performed with the same density of special k-points, \(4 \times 4 \times 1\), in the bulk calculations. The surface structures were constructed using two-dimensional periodic slabs in the x-y plane, containing up to 40 atoms. Larger simulation cells (up to 160 lattice sites) were also considered in some peculiar cases. A slab containing 5 atomic layers was sufficient to represent the CdS (1010) surface since increasing the number of layers up to 7 layers both the surface energy and the interatomic distances showed no remarkable changes. 20 Å of vacuum region separated the image-slabs in the z-direction to avoid any interactions between images due to periodic boundary conditions. Surface vacancies, \(V_{\text{Cd}}\) and \(V_{\text{S}}\), were generated by removing, in turn, one \(\text{Cd}\) and one \(\text{S}\) atom from the top layer. Two non-equivalent positions per ion - top and hollow, respectively - were identified. [13] The whole system, except for the two bottom layers kept fixed to simulate continuous bulk, was then allowed to fully relax until the residual atomic force became less than 10-4 eV/Å. Single molecules of \(\text{O}_2\), \(\text{H}_2\text{O}\) and a combination of them were then placed in different positions of the defective surface, since the defect-free surface was previously shown [14,15] to be unreactive in the presence of the same molecules. The adsorption energy was obtained as the difference between the total energy of the fully relaxed system \((\text{surface} + \text{molecule(s)})\) and the total energies - separately computed - for the defective surface and the single molecules: \(E_{\text{ad}} = E_{\text{surface} + \text{molecules}} - E_{\text{surface}} - \sum E_{\text{molecule}}\).

Thereafter, we focus on the cadmium vacancy in top (henceforth \(V_{\text{Cd}}^{\text{top}} \equiv V_{\text{Cd}}\)) and on sulfur vacancy in hollow (henceforth \(V_{\text{Cd}}^{\text{hollow}} \equiv V_{\text{S}}\)) positions because these sites led to the highest adsorption energies. A possible mechanism of the dissociative recombination of \(\text{O}_2\) and \(\text{H}_2\text{O}\) on top of sulfur and cadmium vacancies, respectively, was studied by means of the Climbing-Image Nudged Elastic Band (CI-NEB) method [16] that is an efficient and robust approach for attempting to find the reaction paths and the saddle points along the minimum energy path (MEP) on the potential energy surface between two endpoints. The MEPs were obtained interpolating a set of seven images including the initial (reactants) and final (products) configurations.

3. Results

\(\text{O}_2 \oplus V_{\text{Cd}}\) - In Fig. 1a the relaxed configuration of \(\text{O}_2\) located above the \(V_{\text{Cd}}\), is shown. The geometry of defective surface in the proximity of the vacancy site changed remarkably. The oxygen molecule is adsorbed on the S atom nearest neighbours (NN) the vacancy creating a bond \(\text{S}-\text{O}_2\) of 1.75 Å. The same S atom, in turn, emerged from the surface and its bond with the \(\text{Cd}\) ion stretched from 2.53 Å to 2.74 Å. The O bond within the oxygen molecule increases from 1.23 Å to 1.32 Å. This position corresponds to an adsorption energy \(E_{\text{ad}}\) as large as \(-0.65 \text{ eV} \approx -62.38 \text{ kJmol}^{-1}\). The bonding charge analysis revealed an accumulation of charge on \(\text{O}_2\) (blue area) and a slight depletion region (green area) on the S ion, as shown Fig. 1b. No spontaneous dissociation was observed in this model, but the strong adsorption energy, the weakening of Cd-S bond and the formation of the \(\text{SO}_2\) group makes this adsorption a first relevant contribution to the understanding of the more complex oxidation reactions that lead to the formation of secondary compounds experimentally observed [2,4,5,7]. The rearrangement of the electron density of the molecule on \(V_{\text{Cd}}\) is highlighted in the study of the density of states.

The corresponding DOS, in Fig. 1c, reveals a well defined peak in the band gap (above the Fermi level, \(E_F\)) due to a residual of the spin-down contribution. The Projected DOS (central and bottom panels) showed that this defect state is due to the superposition of 3p-states of sulfur atoms nearest neighbours and 2p-states of oxygen involved in the binding. They are unoccupied states representing acceptor levels, i.e. electron holes, localised in the S dangling bonds hybridised with \(p\)-states of oxygen. In order to rule out eventual size effects on the geometrical and the electronic structure in the region of the defect a four times larger simulation cell was considered. In the latter system the second shell of vacancy nearest neighbours played a role since the stretching of O-O bond in the oxygen molecule pointed out in the smaller system led to a bond rupture. A remarkable difference noticed is, in fact, the spontaneous dissociative adsorption of \(\text{O}_2\) where (see Fig. 2) we observe the formation of two separate O-S groups after the breaking of \(\text{O}_2\) bond. The distances between \(\text{O}\) and \(\text{S}\) are 1.57 and 1.56 Å for the upper and lower O atoms, respectively. Moreover, the sulfur atom bound to the lower O, sinks of 0.94 Å with respect to the correspondent surface S atoms. As for the electronic structure, there is still an overlap of \(\text{O}\) and \(\text{S}\) \(p\)-states, but the local magnetisation, due to a residual spin asymmetry contribution that is present in the isolated cadmium vacancy [13,17,18], is no longer detected. The Löwdin charge analysis was employed for identifying partial charges on atoms in a periodic system where the electron wave functions are represented by a plane
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