Relazione Scientifica sull'attività svolta nel programma STM

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con qualifica: **Ricercatore livello III**

Dipartimento di afferenza: **Scienze Fisiche e tecnologie della materia**

Titolo del programma: **Novel approach in the study of cadmium yellow pigments degradation**

Obiettivo iniziale (max 500 battute)

The present project focuses on the DFT study of the oxidation mechanism of CdS defective surface covered by oxygen and water. The main goal is the application of the ACBN0 method, developed by the Prof. Buongiorno Nardelli's group, to examine the oxidation state changes of the surface ions and the electron flow during the adsorption and oxidation processes.

Descrizione dei risultati raggiunti e del lavoro avviato attualmente in corso

Introduction - A severe and irreversible alteration process is taking place in both historic and modern synthetic pigments used in impressionist and modern painting from the 1880s through the 1920s, as a consequence of their interaction with external agents present in the environment and with light. In particular, the brilliant yellow pigment takes its colouration from cadmium sulfide (CdS), a II-VI semiconducting compound. The degradation of cadmium yellow occurs primarily in the lighter yellows producing chalking and crumbly surfaces. This alteration was ascribed to an initial photo-oxidation of CdS.
A density functional (DFT) approach, widely and successfully involved in the design of novel materials, was adopted in the studies of ancient pigments to tackle the mechanisms which induce the degradation. At present, the study of optical properties within DFT is prohibitive for large systems. The ACBN0 method, developed by the Prof. Buongiorno Nardelli's group, was demonstrated in some cases, including CdS, to be a suitable and reliable alternative for this purpose with a relatively low computational cost.

Activity and preliminary results – A hierarchy of different codes was setup and used to perform calculations of the clean and defective cleavage surface of CdS. The ACBN0 functional (Gopal et al., Phys. Rev. B 91, 245202 (2015)), a pseudohybrid Hubbard density functional that introduces a new

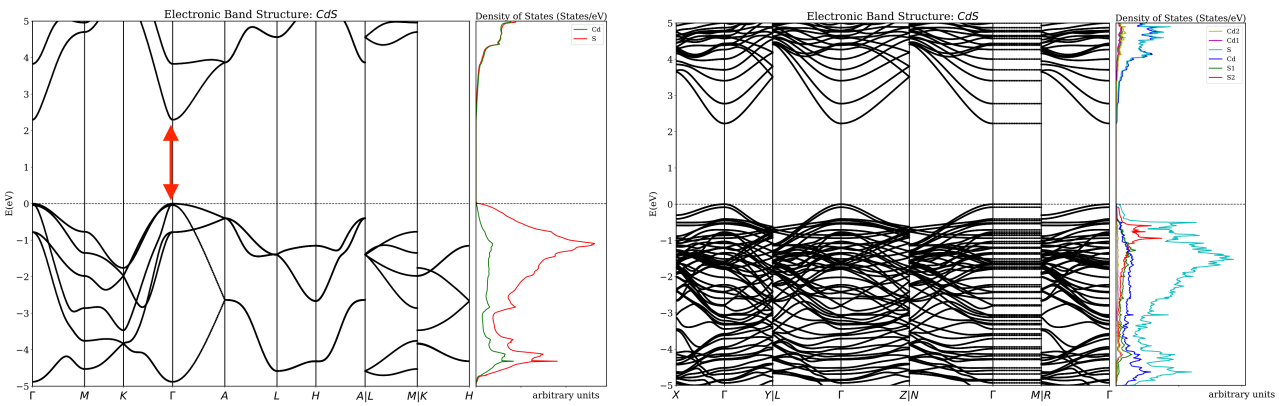

Figure 1 – Band structure and Density of States of CdS bulk (left panel) and (10.1) clean surface (right panel). The dotted line at E=0 represents the Fermi energy at the valence band maximum. The red arrow refers to the direct gap at Γ.

ab initio approach to compute U and J that does not contain any empirical parameter, was successfully applied to the systems previously studied by the applicant with standard DFT-GGA with a significative improvement of the shortcoming typical of DFT, i.e. a severe underestimation of the semiconductor band gap. In Figure 1 the band structure of CdS bulk (left) and surface (right), respectively, obtained with ACBN0 is shown.
The energy gap E_g, direct at **Γ**, resulted as large as 2.30 and 2.23 eV for the CdS bulk and clean surface, respectively, in good agreement with the experimental value of 2.42 eV. The same value obtained with standard DFT-GGA calculation was 50% underestimated (1.19 eV).
As for the study of point defects in both bulk and surface CdS excellent results were obtained for both S and Cd interstitials in the bulk and S and Cd surface vacancies. Figure 2 shows an example of the

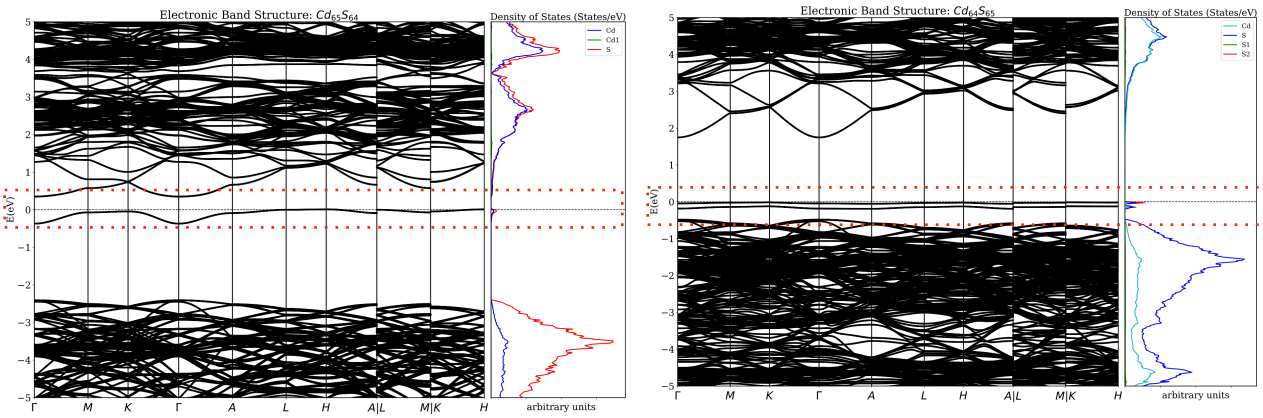

Figura 2 – Band structure and Density of States of S (left panel) and Cd (right panel) interstitial atoms in CdS bulk. The dotted line at E=0 represents the Fermi energy at the valence band maximum. The dotted red frame highlights the localized electron states representing shallow donors (left) and acceptors (right), respectively.

interstitials defects in CdS bulk. In the left panel Cd-intestitial appears to induce shallow donor states in the band structure, below the conduction band minumum, while S-interstitial (right panel) is responsible for shallow acceptor states close to the VBM, as experimentally observed (Cretu *et al*., Appl. Phys. Lett. **110**, 111904 (2017)). The estimate of the dielectric constant, in order to calculate the absorption energies from the defect levels, is still in progress.
The oxidation mechanism of the surface requires a longer computational time and the study is going on at present. The strategy adopted includes the use of a continuum model of dielectric (Andreussi *et al*., J. Chem. Phys. 136, 064102 (2012)) to simulate different solvation effects ontop of both the clean and defective surface where only a limited number of oxygen and water molecules is explicitly taken into account. This approach allows to simulate a more realistic solvent with a low computational cost. In other words, different dielectric constants mimick environments with different relative humidity, typical of those present in museums where the painting are exposed.

The collaboration with the hosting group was definitely stimulating and fruitful. The applicant was invited to give two talks. The first one for the local scientific community at the Department of Physics, University of North Texas (UNT), and the second facing a wider audience of scientists and artists a the University of Texas at Dallas (UT Dallas).
Moreover, a longer scientific visiting at the UNT was proposed to the applicant. It will take place on October 2018 for approximately 3 months.

We already have the draft of *i)* a co-signed manuscript that will be soon ready for submission; *ii*) a proposal submitted to the local institution (UNT) in order to obtain funds useful for travelling from/to the two Institutions (CNR-IOM/UNT); *iii*) a collaboration with the local experimental group already involved in the study of coloured pigments.

Firma del Fruitore