

Density functional theory study of Cyanidin (Cy) dye molecule adsorbed on (100) TiO₂ anatase surface for application in DSSCs

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Abstract. Density functional theory (DFT) has been used to study the geometric, electronic and optical properties of Cyanidin (Cy) dye and its adsorption behaviour on (100) TiO₂ anatase surface. The generalized gradient approximation (GGA) was used in the scheme of Perdew-Burke Ernzerhof to describe the exchange -correlation function as implemented in the CASTEP package in material studio of BIOVIA. Our results show a redshift absorption of cyanidin dye adsorbed on (100) anatase TiO₂ surface, with a shift of Valence band towards the conduction band illustrating the reduction of band gap. The calculated adsorption energy of Cyanidin dye on (100) TiO₂ anatase surface was found to be 24.51 K cal mol⁻¹ suggesting a stable grafting of the cyanidin dye onto the surface of the semiconductor. The highest percentage of light harvesting efficiency was found to be 14% at maximum wavelength. The adsorption results show a spontaneous electron injection followed by efficient regeneration of the oxidized dye molecules by the electrolyte and strong binding ability to the TiO₂ surface.

1. Introduction

The demand for reliable and economically viable alternatives to fossil fuels and the search for low cost renewable energy photovoltaics technologies have boosted the research on new materials. The solar cells used in harvesting the solar power are commonly categorized into different types in respect to the composition of their material (organic solar cells, non-crystal, multiple crystal, and single crystal silicon solar cells). The production cost of the solar cells based on silicon crystal material is high compared to the organic solar cells, which uses low temperature technologies and available materials [1]. The dye sensitized solar cells (DSSCs) is one on the current studied type of solar cells due to its lower cost of manufacturing, flexibility, high photon to energy conversion efficiency and its ability to be used as skylight windows [2]. DSSCs are devices that convert solar to electric energy by light sensitization established on wide energy band gap semiconductors [3]. Typically a DSSCs architecture contains a transparent conductive oxide (TCO) on a glass or plastic substrate, a mesoporous nanocrystalline layer of the semiconductor (TiO₂), a sensitizer monolayer (dye) adsorbed on the surface of the semiconductor, an electrolyte with a redox couple (i.e. I⁻ /I₃⁻) and a metal counter electrode where the redox mediator is regenerated[1-3]. The dye which acts

as sensitizers in DSSCs plays an important task in absorption and conversion of incident light ray to electricity[4,5] . Recently, more attention has been directed to the use of metal-free organic dyes in DSSCs because of no noble metal resource restriction, high molar absorption coefficient, relatively easy synthetic procedure, several structures, tuneable absorption spectral response from the visible to the near infrared area and economical production techniques [6]. In this study we reported on the DFT studies of Cyanidin dye molecule on the (100) TiO₂ anatase surface, we reported our results on the light harvesting efficiency, HOMO-LUMO energy levels for electron injection of the dye, and the optical properties and electronic properties of (100) TiO₂ anatase/Cyanidin dye complex.

2. Computational method

The structure of the dye molecule was built using Material Studio of BIOVIA on a 3D atomic window [7]. The dye molecule structure was cleaned so that the atoms are reoriented in their lattice positions. Geometrical optimization of the dye molecule was performed by CASTEP package in material studio of BIOVIA using density functional theory (DFT) which uses a plane-wave pseudopotential method generalized gradient approximation (GGA) in the scheme of Perdew-Bruke-Ernzerhof (PBE) to describe the exchange-correlation functional using the coarse quality and all band/EDFT as electronic minimizer. The ground state structures obtained through geometrical optimization was imported into a new 3D atomic window and the optical absorption properties were calculated using Material Studio of BIOVIA Vulnerability Analysis Methodology Program (VAMP) [7]. Anatase TiO₂ bulk structure was optimized using CASTEP code within the framework of the Material Studio of BIOVIA to obtain its ground state properties. The GGA-PBE functional were used for geometrical optimizations. The convergence parameters of anatase TiO₂ structure were calculated and the k-points were obtained to be 7 x 7 x 3 and the cut-off energy to be 650 eV, the fixed basis set and ultra-soft pseudopotential were used throughout the study. The ground state structures obtained through geometrical optimization were imported into a new 3D atomic window and the (100) surface was cleaved from the structures and a vacuum slab of appropriate size built for the structures. After this process, the surfaces were optimized using the same convergence parameters obtained for the bulk structures and the electronic and optical properties calculated. The dye/TiO₂ complex were also optimized to obtain the ground state structures, and the electronic properties calculated using CASTEP code

3. Results and discussion

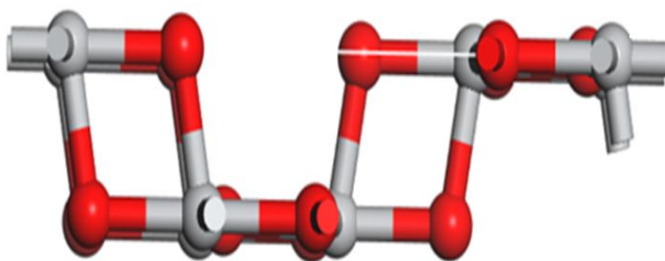


Figure 1: Structure of TiO₂ anatase (100) surface, red represent oxygen and grey represent titanium
Figure 1 illustrate the structure of TiO₂ anatase (100) surfaces cleaved from anatase TiO₂ bulk structure. The atoms in this surface are having some cleaved bonds in the termination position, while terminating with both oxygen and titanium. The surfaces were optimized by relaxing atoms to eliminate surface tension.

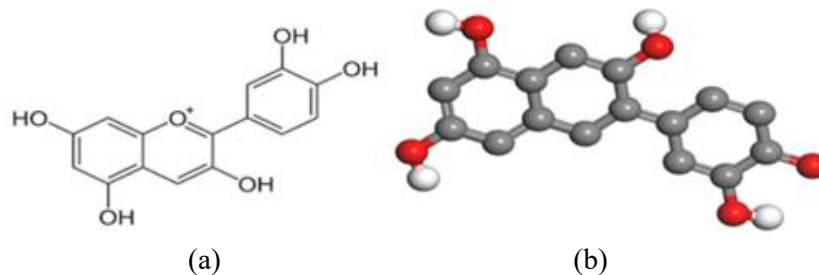


Figure 2: The molecular structure of Cyanidin dye molecule [6] (a) and optimised geometry structure, red balls represent oxygen, grey balls represent carbon, and white balls represent hydrogen.

The molecular structure of Cyanidin dye molecule is shown in figure 2, it is understandable that this dye has a widely delocalized p-conjugate electronic system on its skeleton plane and a highly symmetric structure [8].

3.1. Energy levels and isodensity surfaces of the dyes

The cyanidin sensitizer dye molecules structure was optimized for ground state energy level in vacuum and the E_{HOMO} , E_{LUMO} and HLG ($E_{\text{LUMO}} - E_{\text{HOMO}}$) were obtained as follows: $E_{\text{HOMO}} = -8.081$ eV, $E_{\text{LUMO}} = -6.424$ eV and HLG = 1.657 eV respectively.

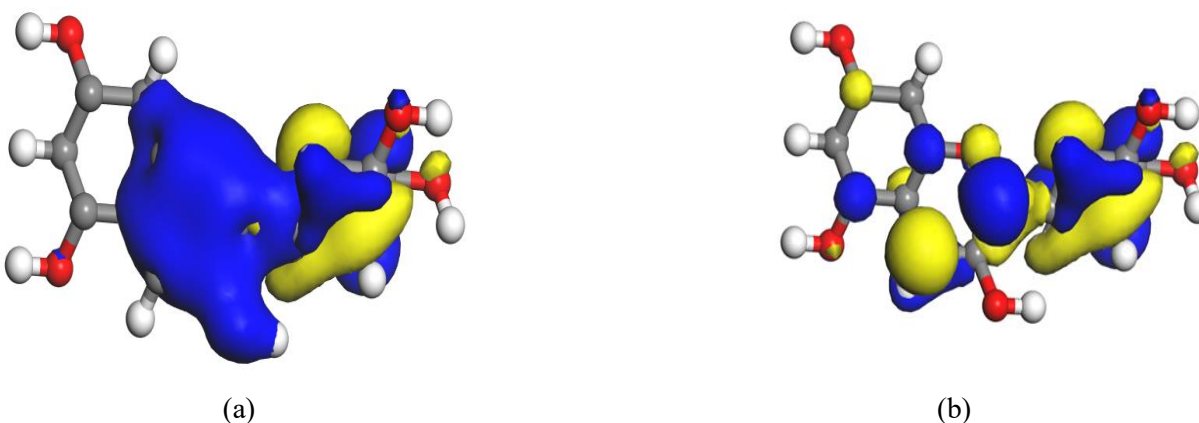


Figure 3: Isodensity surfaces of the molecular orbitals (a) highest occupied molecular orbital (b) lowest unoccupied molecular orbital of Cyanidin dye molecule

The lower value of the HOMO-LUMO energy gap of sensitizer, illustrate the enhancement absorption of dye at higher wavelength and photocurrent response of DSSCs. Usually the energy gap between the LUMO of the dye and the conduction band must be more than 0.2 eV for effective electron injection. The calculated results show that the LUMO energy level of cyanidin dye is higher than the TiO_2 conduction band edge (4.0 eV) and energy gap between them is more than 0.2 eV. Thus, cyanidin has strong ability to inject electron into TiO_2 conduction band.

3.2. Absorption spectrum and light harvesting efficiency of the Dyes

Figure 4 illustrates UV-Vis spectra of Cyanidin dye molecules obtained using VAMP code on material studio package. The absorption maxima of the cyanidin dye molecules is situated at 304 nm.

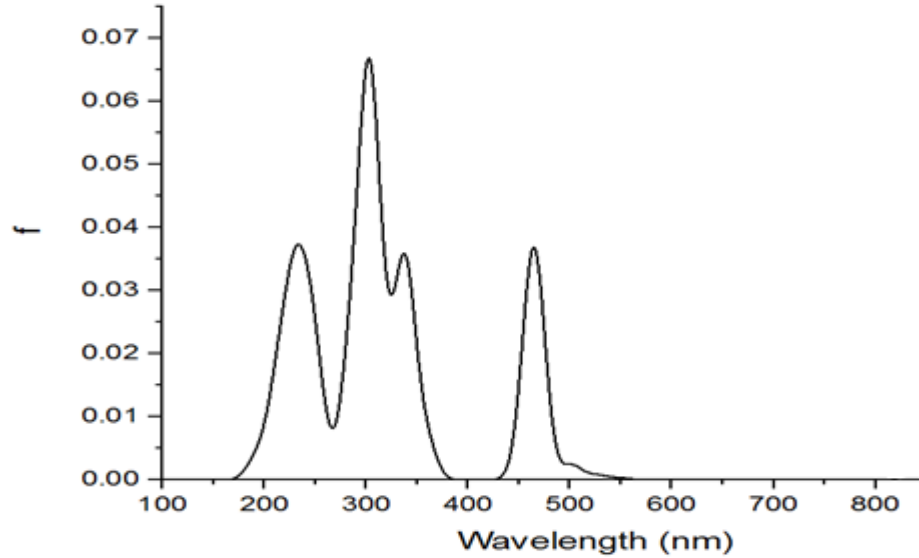


Figure 4: Calculated UV-Vis spectrum for cyanidin dye molecule

The light harvesting efficiency (LHE) at the absorption peaks was calculated using the following equation: $LHE(\lambda) = 1 - 10^{-f}$ where f denotes the absorption or the oscillator strength of sensitizer at a given wavelength (λ) [9]. LHE becoming 0 for zero oscillator strength and 1 for infinite oscillator strength. The LHE values of Cyanidin dye calculated at respective λ_{max} are shown on table 1. It can be observed from the figure 4 and table 1 that the highest absorption of the dye molecule is at 304 nm with the LHE percentage of 14.0 which shows that the cyanidin adsorb more photons at visible light.

Table 1. Calculated light harvesting efficiency of cyanidin dye molecule

Wavelength	f	LHE	LHE (%)
235	0.037	0.082	8.20
304	0.066	0.140	14.0
339	0.035	0.077	7.70
464	0.036	0.081	8.10

3.3. Adsorption of cyanidin dyes on TiO_2 anatase (100)

Figure 5 shows the cyanidin dye adsorbed on TiO_2 anatase (100) surface to form TiO_2 /dye complex, which is the structure formed when the dye molecule is adsorbed on the surface of TiO_2 , the substance being absorbed is an adsorbate and the absorbing substance, an adsorbent. In this study an adsorbate is a cyanidin dye molecule and the adsorbent is TiO_2 anatase (100) structure.

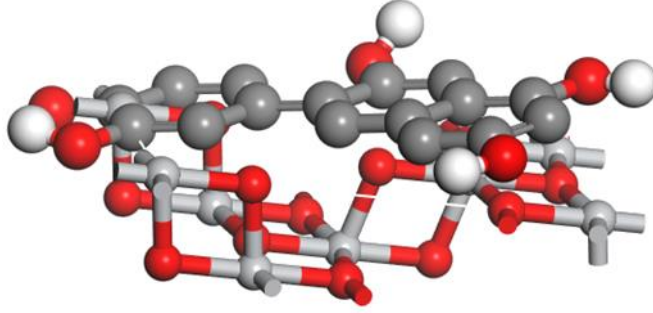


Figure 5: Structure of Cyanidin dye molecule adsorbed on TiO₂ anatase (100) surface

3.3.1. Electronic property (Density of State)

The total density of states (TDOS) shown in figure contains broad surface valence band and conduction bands separated by a wide band gap for TiO₂ anatase (100). A great TDOS at a given energy state means that there are numerous available states for occupation by electrons while a TDOS of zero represents that there are no states that can be occupied by electrons.

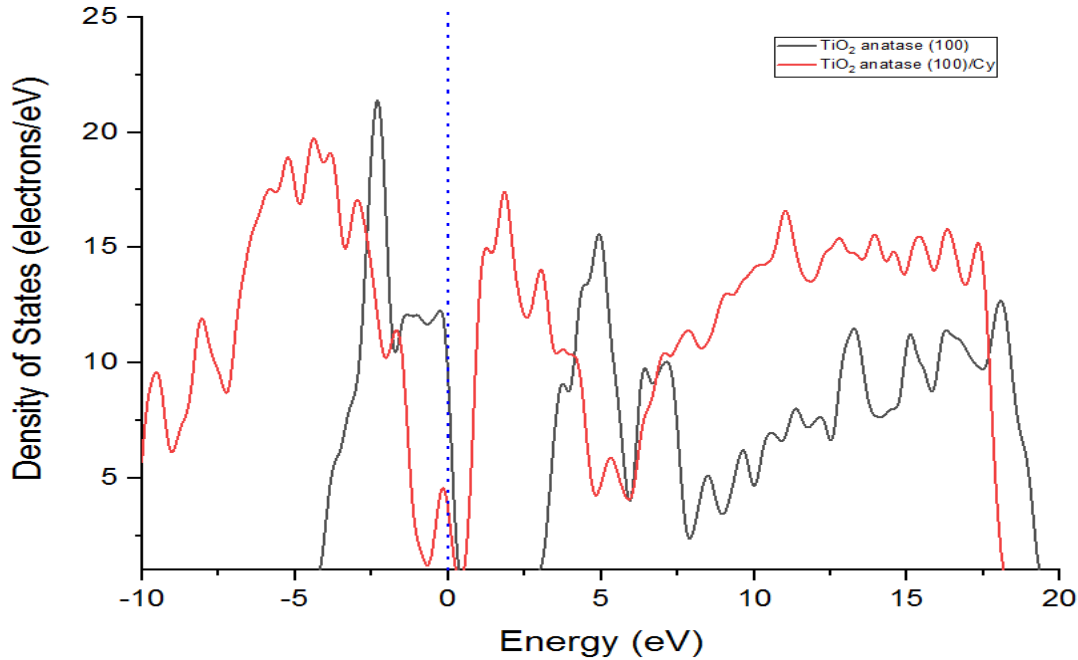


Figure 6: The total density of states of TiO₂ anatase (100) and TiO₂ anatase (100)/Cy complex

The TDOS curves Figure 6, shows that after adsorption, the dyes introduce sharp occupied molecular energy levels in the band gap. When comparing the pure TiO₂ anatase (100) surface to the TiO₂ anatase (100)/Cyanidin complex, the TDOS, point out a shift of the conduction band edge of TiO₂ towards the valence band, hence the band gap of TiO₂ anatase (100)/Cyanidin complex is smaller than that of the pure TiO₂ anatase (100) surface.

3.4. Adsorption energy of TiO₂ /dye complex

The adsorption energies of cyanidin on TiO₂ are computed using equation 2 [9]:

$$E_{ads} = [E_{dye} + E_{(TiO_2)}] - [E_{(dye+TiO_2)}]$$

where E_{ads} is the adsorption energy, E_{dye} is the energy of the dye, $E_{(TiO_2)}$ is the energy of the TiO₂ slab

and $E_{(dye+TiO_2)}$ is the total energy of the dye-TiO₂ complex [9]. The calculated adsorption energy was found to be 24.51 K cal mol⁻¹. The adsorption energy denotes the binding ability of the dye molecules, and the positive value obtained shows that Cyanidin binds stronger when adsorbed on to TiO₂ anatase, and the TiO₂/dye complex is stable.

4. Conclusion

First-principles DFT has been used to systematically investigate, the HOMO-LUMO energy gap, UV-Vis spectrum and light harvesting efficiency of cyanidin dye molecules. The HOMO-LUMO energy gap found to be 1.657 eV, which shows an effective electron injection and the shift of the absorption to near infrared region. The calculated results show that light harvesting efficiency depend on the absorption (oscillator strength) of the dyes. The obtained adsorption energy of cyanidin dye on anatase TiO₂ (100) surface clearly points out to large value of around 24.51 K cal mol⁻¹ which shows that the complex is stable and has a strong binding ability., The TDOS illustrate that after adsorptions, the dyes introduce sharp occupied molecular energy levels in the band gap.

5. Acknowledgement

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6. References

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