

Full length article

Role of surface defects on the adsorption of poly(9-vinylcarbazole) on TiO₂ using the monomer as a donor:acceptor modelDominique Mombrú^a, Mariano Romero^{a,*}, Mario G. Sandoval^{a,b}, Ricardo Faccio^{a,*}, Álvaro W. Mombrú^{a,*}^a Centro NanoMat/CryssMat/Física, DETEMA, Facultad de Química, Universidad de la República, C.P. 11800 Montevideo, Uruguay^b Instituto de Física Del Sur (IFISUR, UNS – CONICET) and Departamento de Física, Universidad Nacional Del Sur, Av. Alem 1253, B8000CPB, Bahía Blanca, Argentina

ARTICLE INFO

Keywords:

Solar cells
Donor
Acceptor
PVK
TiO₂
DFT

ABSTRACT

In this report, we studied the interaction between 9-vinylcarbazole (VK) –i.e. the monomer of poly(9-vinylcarbazole) (PVK)– and a TiO₂ (101) surface in order to shed some light in the interface phenomena of this promising fullerene-free donor:acceptor system as active layer for solar cells. Since the role of the TiO₂ surface defects is the main concern of our study, we proceeded to simulate the adsorption of the molecule on TiO₂ with oxygen or titanium atom vacancies and without any defect. All these systems were studied using First Principles calculations, utilizing Density Functional Theory (DFT). The adsorption energy of the VK monomer-TiO₂ systems was favorable in all cases. The presence of vacancies in the TiO₂ surface yielded modifications in the electronic properties: the difference between the LUMO level of VK and the conduction band of TiO₂-O surface is only ~0.2 eV, thus allowing to infer a decrease in the energy barrier associated to the injection of electrons from VK monomer towards the TiO₂-O surface. The charge density differences in all systems also revealed that the donor:acceptor model is plausible and concurs with previous results, suggesting promising features for potential application as a donor:acceptor systems in fullerene-free solar cells.

1. Introduction

After the first appearance of polymer donor:acceptor heterojunction systems as active layers materials for solar cell applications [1–3], there has been a lot of effort focused in the preparation of different materials pursuing the enhancement of the photovoltaic performance [4–6]. The more popular electron donor polymers are typically poly(carbazole) or poly(thiophene) and their derived polymers [1–8]. On the other hand, the most common electron acceptor is [6,6]-phenyl-(C71 or C61)-butyric acid methyl ester (PC61BM or PC71BM) fullerene due to their high electron affinity and mobility [1–8]. However, these acceptor materials are expensive and possess low absorption in the visible spectra, making them nonideal candidates for technological applications. In the last years, non-fullerene acceptors have been thoroughly studied pursuing higher visible light absorption and lower costs of fabrication [9–13]. Moreover, inorganic nanoparticles fillers such as titanium oxide (TiO₂) in its anatase polymorph have been already reported as promising acceptor materials for safer and lower cost hybrid solar cells [14–18]. In our case, we have recently shown that for TiO₂ nanoparticles sizes confined down to ~3 to 7 nm size, the experimentally observed behavior was as excellent acceptors when loaded to a poly(vinyl carbazole)

(PVK) donor host, probably due to the increment of the effective interface between both materials [19]. Our main goal in the present manuscript is to unravel the interface phenomena behind the electronic interaction of this promising donor:acceptor system by means of Density Functional Theory (DFT) calculations. Interesting theoretical approaches of different chemically bonded chromophore molecules onto TiO₂ surface has recently shed some light on the donor:acceptor electronic interactions in these systems [20–22]. However, there is a recent study of the proximity effects of unbonded acceptors such as polycyclic aromatic hydrocarbons onto TiO₂ surface, revealing that donor:acceptor coupling do not always require covalent bonding [23]. In the present manuscript, we will theoretically study the electronic interactions of a chemically unbonded PVK monomer and a TiO₂ surface studying the effect of the presence of atom vacancies at the surface, in an effort to get a better approximation to a more realistic experimental situation.

2. Computational method

The purpose of the work is to simulate the adsorption of poly(9-vinylcarbazole) (PVK) on TiO₂ (101) surface; for that reason, we started

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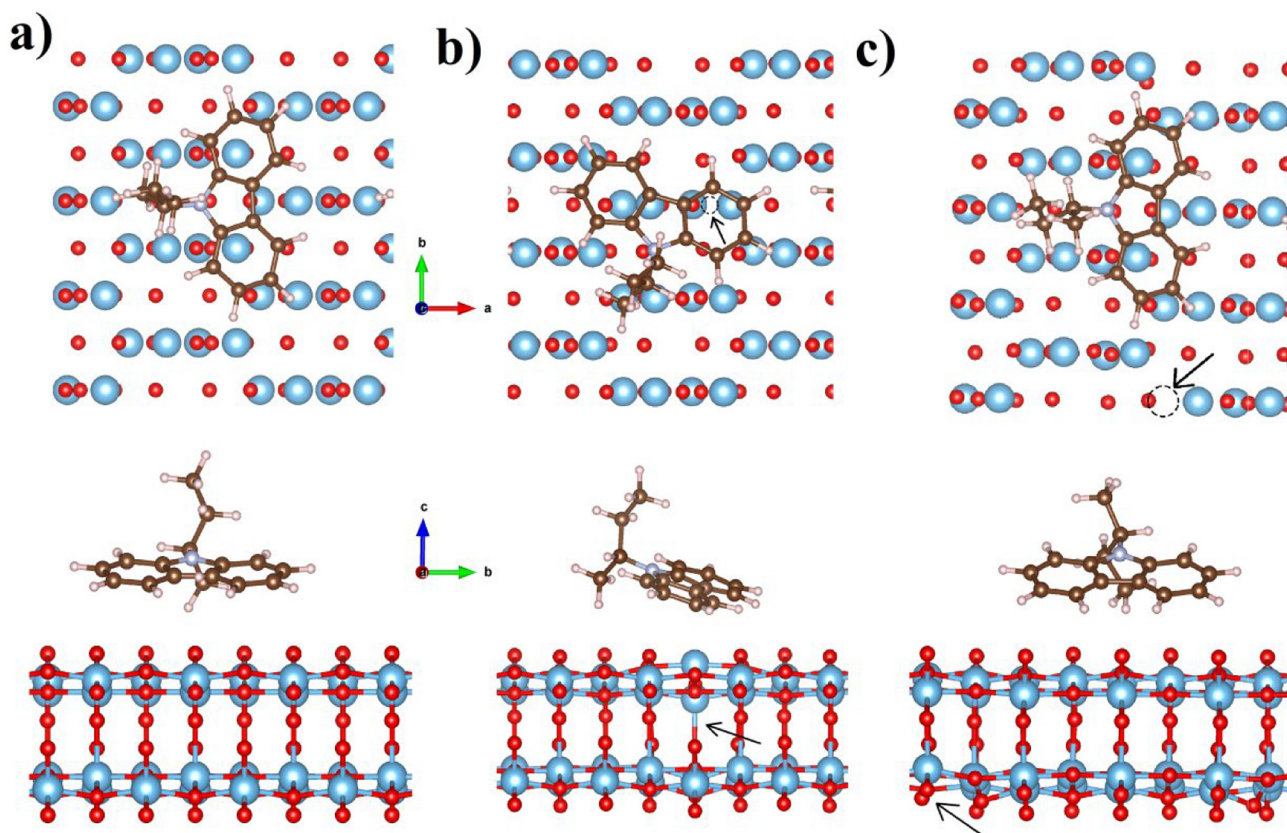


Fig. 1. Optimized structures for a) TiO_2/VK b) $\text{TiO}_2\text{-O}/\text{VK}$ and c) $\text{TiO}_2\text{-Ti}/\text{VK}$ system with different perspectives. Arrows show the vacancies sites.

Table 1

Average distances and adsorption energy for TiO_2/VK , $\text{TiO}_2\text{-O}/\text{VK}$ and $\text{TiO}_2\text{-Ti}/\text{VK}$ systems.

	Distances (Å)	Adsorption energy (eV)
TiO_2/VK	$d = 3.71$	-0.17
$\text{TiO}_2\text{-O}/\text{VK}$	$d = 3.54$	-0.88
$\text{TiO}_2\text{-Ti}/\text{VK}$	$d = 3.62$	-1.09

the optimization separately, for the molecule model –i.e. the monomer, named VK- and the surface. In the case of the VK we performed a full geometrical optimization. In the case of the surface, due to the fact that the most stable nanoparticle consists in anatase, and the (101) is the most favorable surface, in terms of surface energy, we decided to build a slab model of anatase- TiO_2 (101) [24]. This slab model consists in a unit cell with $a = 10.5$ Å, $b = 14.9$ Å and $c = 27.1$ Å, having a vacuum space of 15 Å aligned along the c-axis, see Fig. 1. The structure was fully optimized in the atomic positions, until reaching a force down to 0.01 eV/Å. In particular, for the anatase TiO_2 (101) surface we considered three different situations, without and with vacancies, one titanium and one oxygen vacancies in the surface, named as $\text{TiO}_2\text{-Ti}$ and $\text{TiO}_2\text{-O}$, respectively. The non-defected structure presents and stoichiometry of $\text{Ti}_{32}\text{O}_{64}$, $\text{TiO}_2\text{-Ti}$ structure presents $\text{Ti}_{31}\text{O}_{64}$ and $\text{TiO}_2\text{-O}$ one presents a $\text{Ti}_{32}\text{O}_{63}$. After achieving the optimization of the VK model and the three different optimized/reconstructed surfaces, we proceeded with the VK adsorption on anatase TiO_2 (101) surfaces, allowing all the atomic positions to relax again. All the calculations were performed utilizing Density Functional Theory (DFT) [25,26] with the VASP code [27–30] (Vienna ab initio simulation package). Pseudopotentials were applied with a plane-wave basis set with a projector augmented wave (PAW) method [31], using a generalized gradient approximation (GGA) as the exchange-correlation functional according to Perdew-Burke-Ernzerhof (PBE) [32,33]. The employed

pseudopotentials correspond to the following configurations: $3s^2 3p^6 3d^2 4s^2$ for titanium, $2s^2 2p^4$ for oxygen, $2s^2 2p^3$ for nitrogen, $2s^2 2p^2$ for carbon and $1s^1$ for hydrogen atoms. The k-point mesh was taken equivalent to $2 \times 2 \times 1$ for the full Brillouin Zone (vacuum space along c-axis), and an energy cutoff of 400 eV was utilized to expand the Kohn–Sham orbitals into plane wave basis sets. The structures were optimized again until the forces in all the atoms were lower than a tolerance value of 0.01 eV/Å. Dipole corrections were applied along the direction perpendicular to the surface.

3. Results and discussion

3.1. Geometry

The optimized structures of TiO_2/VK without vacancy, with O vacancy ($\text{TiO}_2\text{-O}/\text{VK}$) and Ti vacancy ($\text{TiO}_2\text{-Ti}/\text{VK}$) systems are shown in different perspectives in Fig. 1. In the three relaxed systems, the aromatic and pyrrole rings of VK are located almost parallel to the TiO_2 surface. For all cases, there is a slight deviation from parallelism for the VK with respect to TiO_2 surface, especially due to steric effects of vinyl moiety of VK. In order to have a rough comparison between all cases, we show the average carbon-oxygen distances, as an approximation to the VK-to- TiO_2 lowest distance for all adsorbed systems, in Table 1. For this purpose, we define this distance by considering the carbon atoms of the aromatic and pyrrole ring of the VK molecule and the oxygen atoms of the TiO_2 surface. In the non-vacancy system, the average carbon-oxygen distances is 3.71 Å, while for oxygen and titanium vacant systems the same average distances are 3.54 and 3.62 Å, respectively. This suggests that both oxygen and titanium defects on TiO_2 systems slightly improves the VK molecule adsorption, as expected. Apart from the slightly different values observed in each case, it is evident that distances, in all structures, are small enough to allow us to consider this interaction as real adsorptions of the molecule. Nevertheless, this will

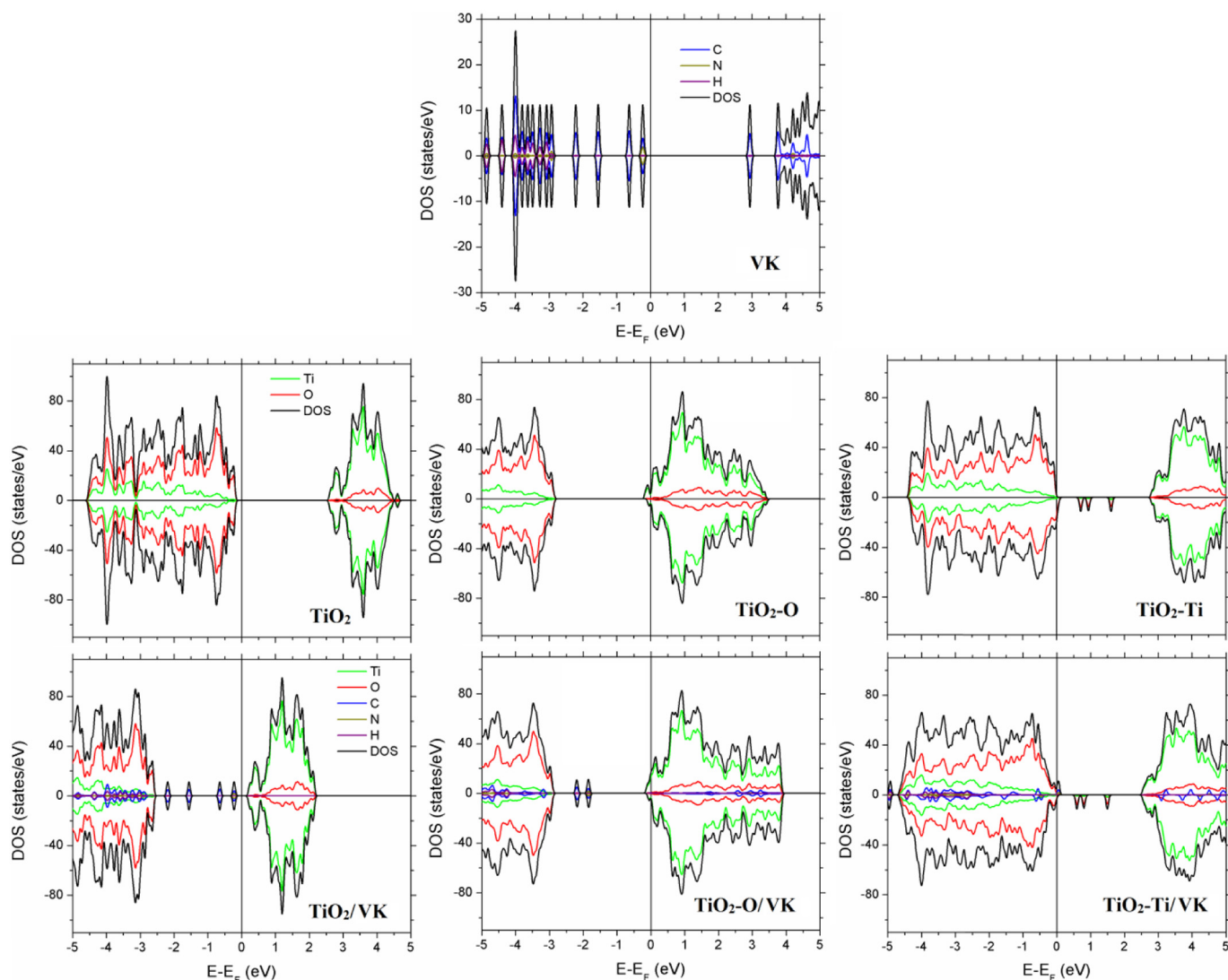


Fig. 2. Density of states (DOS) for all structures. Each atom contribution is represented with the selected colors assigned in each label.

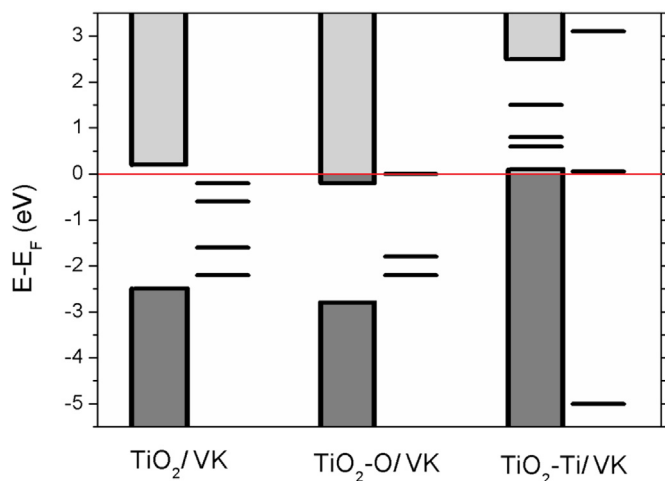


Fig. 3. Schematic energy level diagram for TiO_2/VK , $\text{TiO}_2\text{-O}/\text{VK}$, $\text{TiO}_2\text{-Ti}/\text{VK}$ systems.

be discussed again when analyzing the adsorption energy and the charge density transfer upon adsorption for all cases in the following sections. It is also interesting to remark that the position of the vacancy

in $\text{TiO}_2\text{-Ti}/\text{VK}$ and $\text{TiO}_2\text{-O}/\text{VK}$ systems produces a slight reconstruction of the original $\text{TiO}_2(110)$ surface. In the case of $\text{TiO}_2\text{-O}/\text{VK}$, the oxygen vacancy slightly moves from the surface into the TiO_2 structure along the c-direction, while in the case of $\text{TiO}_2\text{-Ti}/\text{VK}$, the titanium vacancy slightly moves along the b- and c-direction as depicted in Fig. 1b and c.

3.2. Total energy analysis

In order to analyze the adsorption process, the corresponding adsorption energies for all structures were calculated according to the following expression, and presented in Table 1:

$$E_{\text{ads}} = E_{\text{TiO}_2\text{-X}/\text{VK}} - (E_{\text{TiO}_2\text{-X}} + E_{\text{VK}})$$

where $E_{\text{TiO}_2\text{-X}}$ is the total energy for isolated $\text{TiO}_2(101)$ surface with non-vacancy, X = O and X = Ti for oxygen and titanium vacancy, respectively, E_{VK} is the isolated VK monomer total energy and $E_{\text{TiO}_2\text{-X}/\text{VK}}$ is the $\text{TiO}_2\text{-X}/\text{VK}$ total energy with non-vacancy, X = O and X = Ti for oxygen and titanium vacancy, respectively. The calculated adsorption energies for non-vacancy, oxygen and titanium vacancy systems were $E_{\text{ads}} = -0.17$, -0.88 and -1.09 eV, respectively; all of them are lower than zero, suggesting a favorable process in all the cases. When comparing the E_{ads} values among them, the most favorable adsorption processes are observed for the $\text{TiO}_2\text{-Ti}/\text{VK}$ system, followed by the $\text{TiO}_2\text{-O}/\text{VK}$ system, being less favorable for the non-vacancy system.

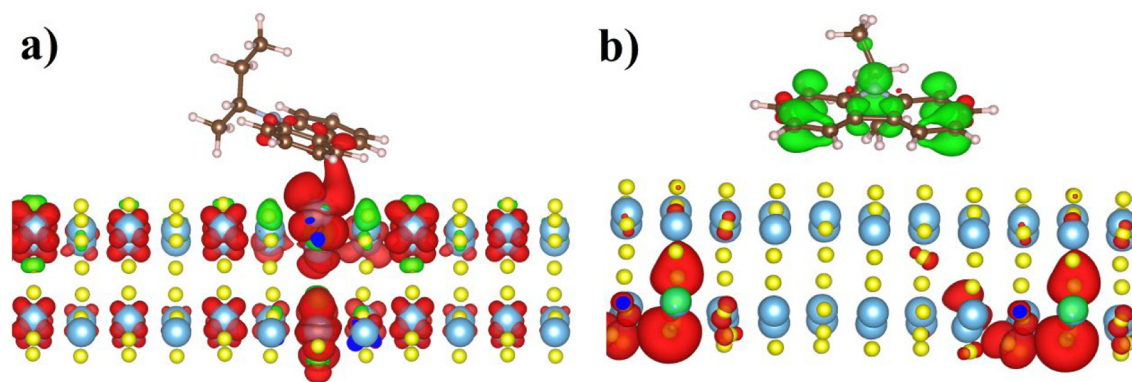


Fig. 4. Spin density maps represented with isosurfaces at 50% of maximum value are represented, where red and green represents spin-up and -down contribution respectively. For a) $\text{TiO}_2\text{-O/VK}$ and b) $\text{TiO}_2\text{-Ti/VK}$ systems.

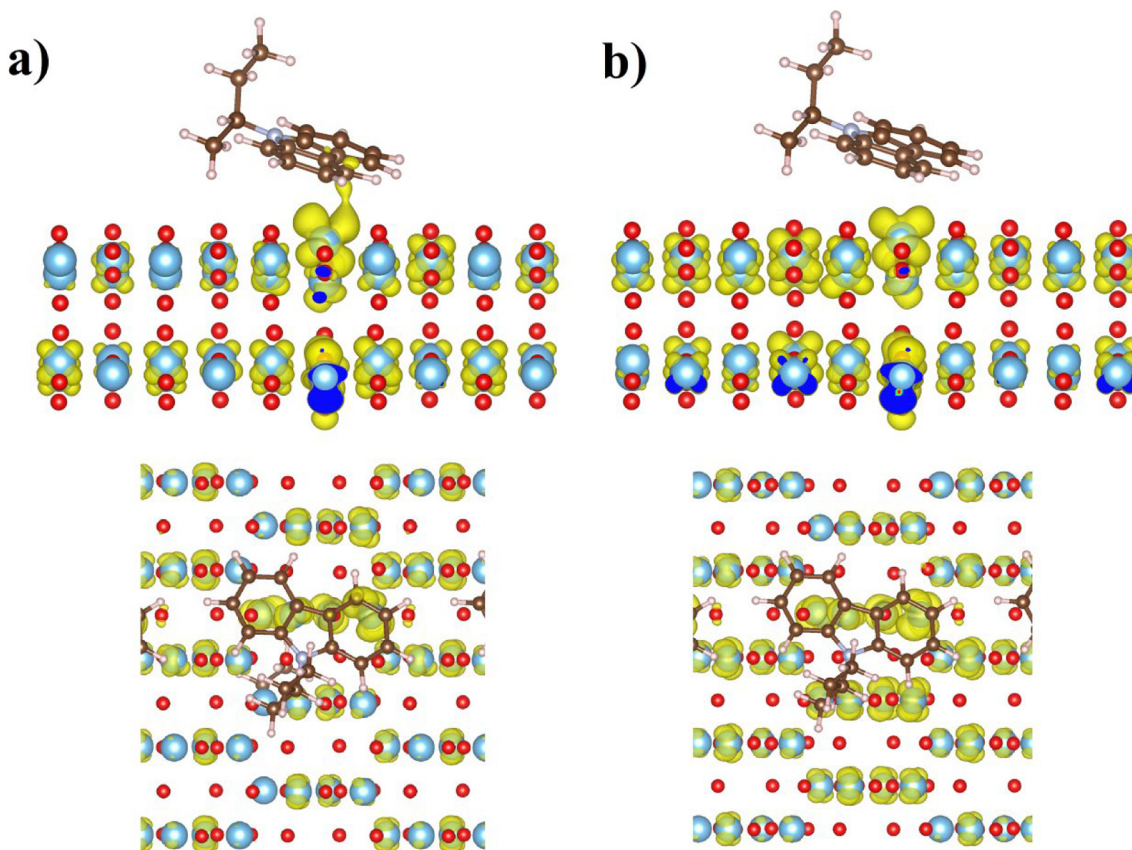


Fig. 5. The charge density associated of the single electron wavefunctions, corresponding to a) -0.05 to 0.00 eV and b) 0.00 to 0.05 eV energy ranges for $\text{TiO}_2\text{-O/VK}$ system in side view (up) and top view (down).

This trend is somehow expected, since the presence of vacancies destabilizes the surface, favoring the VK adsorption process. Additionally, our values concur with E_{ads} values reported for anatase (101) surfaces with other chemically anchored chromophore molecules, with values ranged from -0.6 to -1.3 eV [20–22,34,35] and also with chemically unbonded polycyclic aromatic hydrocarbon (PAH) molecules, which yielded down to -2.1 eV values [23]. It was already observed that the presence of oxygen vacancies also leads to an increment of the adsorption onto TiO_2 anatase (101) surface [21] but to our knowledge, there are no reports about similar systems with titanium vacancies.

3.3. Electronic structure

In order to discuss the electronic structure of the system, we start

presenting the density of electronic states (DOS) plots for TiO_2 , VK and $\text{TiO}_2\text{/VK}$ structures without vacancy and with O and Ti vacancies, which are shown in Fig. 2. The DOS for the isolated non-vacancy TiO_2 system presented a typical semiconductor behavior with a main contribution of oxygen (O-p states) and titanium (Ti-d states) for the valence and conduction band, respectively. The isolated non-vacancy TiO_2 surface showed an energy gap of ~ 2.7 eV, in good agreement with the typical ~ 3.0 eV band gap values calculated for anatase TiO_2 in previous reports [24,36]. Upon the adsorption of the VK monomer, the Fermi level shifts close to the TiO_2 surface conduction band edge yielding to an n-type semiconducting behavior. This could be suggesting that the VK monomer is acting as an electron donor promoting the electronic doping of the TiO_2 surface but this will be further analyzed in the next section. In the case of the oxygen vacancy system, the

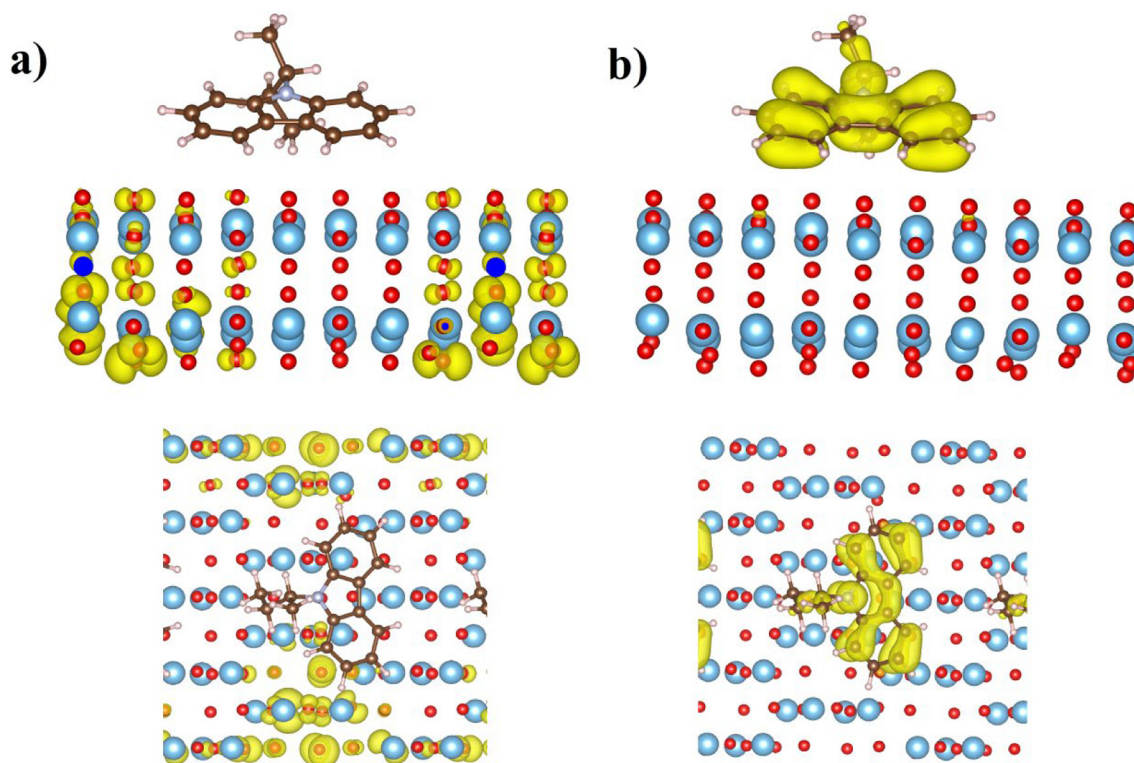


Fig. 6. The charge density associated of the single electron wavefunctions, corresponding to a) -0.05 to 0.00 eV and b) 0.00 to 0.05 eV energy ranges for $\text{TiO}_2\text{-Ti/VK}$ system in side view (up) and top view (down).

difference between the valence band maximum and the conduction band minimum of TiO_2 surface is ~ 2.6 eV for the isolated $\text{TiO}_2\text{-O}$ surface and $\text{TiO}_2\text{-O/VK}$ system, showing a slight shift of the TiO_2 surface conduction band minimum below the Fermi level, as depicted in Fig. 3. Moreover, the LUMO energy level of the VK monomer shifted to lower energy values when interacting with the $\text{TiO}_2\text{-O}$ surface, as depicted in Fig. 3. The difference between the LUMO level of VK and the conduction band of $\text{TiO}_2\text{-O}$ is only ~ 0.2 eV, thus allowing to infer a decrease in the energy barrier associated to the injection of electrons from VK towards the $\text{TiO}_2\text{-O}$ surface. In the case of the titanium vacancy system, the difference between the valence band maximum and conduction band minimum for the TiO_2 surface is ~ 2.6 eV and ~ 2.3 eV, for the isolated $\text{TiO}_2\text{-Ti}$ surface and the $\text{TiO}_2\text{-Ti/VK}$ system, respectively. However, the valence band maximum of TiO_2 surface shifted close below the Fermi level and the LUMO energy level of the VK monomer is slightly above the Fermi level, as depicted in Fig. 3. The previous results indicate that the charge injection at the $\text{PVK}:\text{TiO}_2$ interface could be drastically enhanced, especially in the presence of oxygen vacancies. Although an enhancement in the charge injection at the $\text{PVK}:\text{TiO}_2$ interface was also experimentally observed for $\text{PVK}:\text{TiO}_2$ nanocomposites by means of dc and ac electrical transport studies, the presence of vacancies in TiO_2 surface has not been discussed in depth experimentally [16,18,19]. In addition, both titanium and oxygen vacancy systems presented unbalanced density of states (DOS) diagram in the corresponding spin-up and spin-down contribution. In the $\text{TiO}_2\text{-O/VK}$ system, the difference in the spin-up and spin-down contribution in the density of states is mainly attributed to the $\text{TiO}_2\text{-O}$ surface with a small contribution of the VK monomer, meanwhile the difference in the $\text{TiO}_2\text{-Ti/VK}$ system is related to both the $\text{TiO}_2\text{-Ti}$ surface and the VK molecule.

3.4. Magnetic ordering analysis

The spin-densities, obtained as $\rho^{up}(\vec{r}) - \rho^{down}(\vec{r})$, for $\text{TiO}_2\text{-O/VK}$

and $\text{TiO}_2\text{-Ti/VK}$ systems are shown in Fig. 4. In the case of $\text{TiO}_2\text{-O/VK}$, shown in Fig. 4a, the spin-density is mainly located in the $\text{TiO}_2\text{-O}$ surface with a minor contribution in the VK molecule which is in agreement with the corresponding DOS, where the difference of the spin-up and spin-down density of states could be attributed mostly to the Ti and O contributions. On the other hand, in the case of $\text{TiO}_2\text{-Ti/VK}$ system, the spin-density is mainly located at the $\text{TiO}_2\text{-Ti}$ surface and also in the molecule, which could suggest that the interaction between them produces an unbalance in the spin of the whole system. The magnetic moments for the $\text{TiO}_2\text{-O}$ surface and for the $\text{TiO}_2\text{-O/VK}$ system have the same value, $1.03 \mu_B$. In the case of the $\text{TiO}_2\text{-Ti}$ surface the magnetic moment is $4.11 \mu_B$ while $\text{TiO}_2\text{-Ti/VK}$ system shows a magnetic moment of $2.00 \mu_B$. The non-vacancy system presented no magnetic moment because there is no defect causing a magnetization in the TiO_2 surface, since there is no electronic-spin unbalance that could contribute to a magnetic ordered state. On one hand, in the $\text{TiO}_2\text{-O/VK}$ system, the magnetic moment is produced by the Ti contribution with $0.12 \mu_B$ and $0.23 \mu_B$ caused by two titanium atoms in the surroundings of the O-vacancy of the TiO_2 surface. On the other hand, in the $\text{TiO}_2\text{-Ti/VK}$ system, the total magnetic moment is mainly produced by the oxygen atoms in the surroundings of the Ti-vacancy of the TiO_2 surface, with 1.12 , 0.44 and $0.43 \mu_B$. All these values are in agreement with DOS presented in Fig. 2, where spin-up and spin-down unbalance are attributed to the titanium atoms for $\text{TiO}_2\text{-O/VK}$ system and to oxygen atoms in the $\text{TiO}_2\text{-Ti/VK}$ system. The presence of a non-zero magnetic moment due to the presence of vacancies has been also recently observed experimentally for bulk and nano- TiO_2 in its anatase polymorph [37,38].

3.5. Charge density analysis

The charge density associated to the single electron wavefunctions, corresponding to -0.05 to 0.00 and 0.00 to 0.05 eV energy ranges of $\text{TiO}_2\text{-O/VK}$ and $\text{TiO}_2\text{-Ti/VK}$ systems are represented in Figs. 5 and 6,

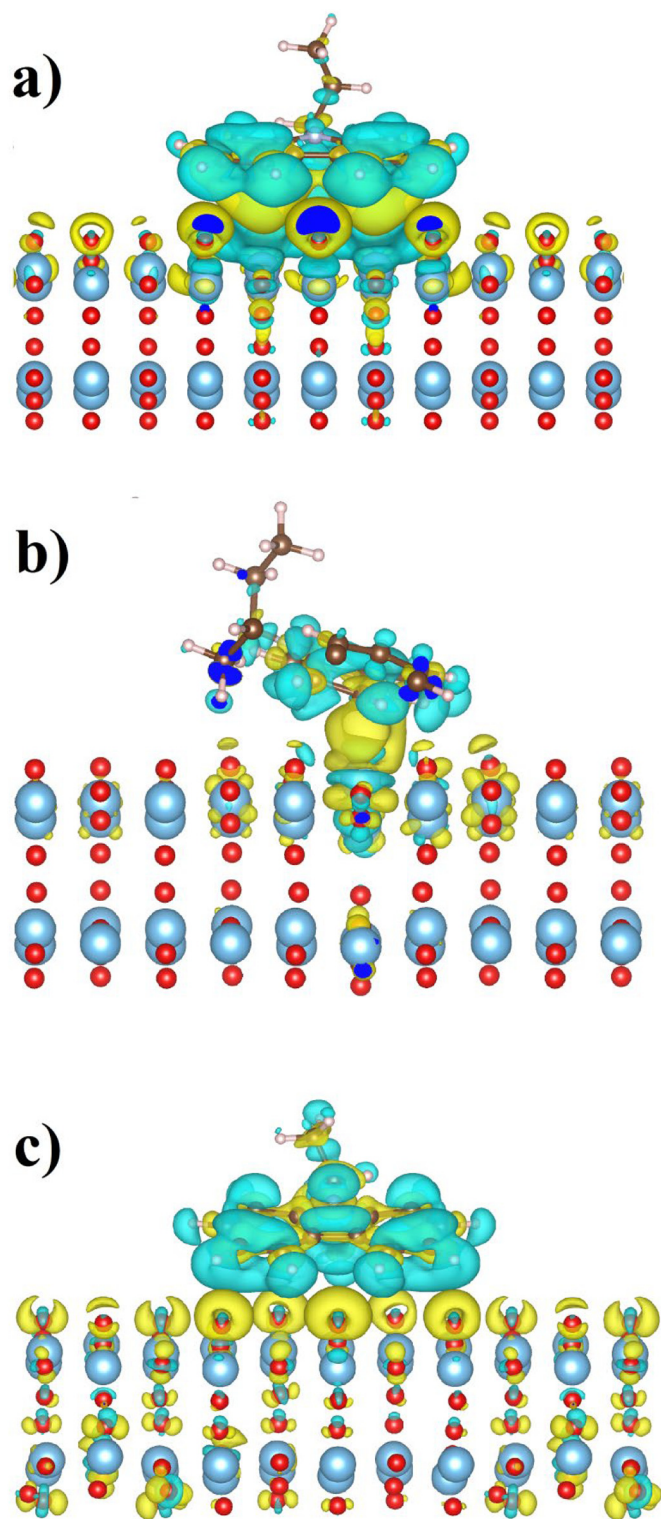


Fig. 7. Charge density differences for a) non-vacancy system (TiO_2/VK), b) oxygen vacancy system ($\text{TiO}_2\text{-O}/\text{VK}$) and c) titanium vacancy system ($\text{TiO}_2\text{-Ti}/\text{VK}$) where the loss and gain of electron density is represented in blue and yellow, respectively.

respectively. In the $\text{TiO}_2\text{-O}/\text{VK}$ system, the main charge density is observed in the titanium atoms of the TiO_2 surface in the whole range. In the $\text{TiO}_2\text{-Ti}/\text{VK}$ system, the main charge density is observed in the oxygen atoms of the TiO_2 surface in the -0.05 to 0.00 eV energy range while in the 0.00 to 0.05 eV range the main charge density is observed

in the molecule, especially in the aromatic and pyrrole rings. This is in agreement with the DOS in the selected energy range, where the main contribution is generated because of the oxygen atoms of TiO_2 surface below the Fermi level and by the nitrogen and carbon atoms of the VK monomer in the other energy range. The difference in the charge density for all surface-monomer interactions are represented in Fig. 7, where the gain and loss of electron density is presented in yellow and blue, respectively. The charge density difference was calculated with the following expression:

$$\Delta\rho(\vec{r})_{\text{ads}} = \rho(\vec{r})_{\text{TiO}_2\text{-X}/\text{VK}} - (\rho(\vec{r})_{\text{TiO}_2\text{-X}} + \rho(\vec{r})_{\text{VK}})$$

In all cases, there is an evident gain of electron density at the TiO_2 surface, while the VK monomer showed a loss of the electron density. This fact suggests that the TiO_2/VK junction acts as a good acceptor:donor system and this behavior do not seem to be drastically modified with the presence of titanium or oxygen vacancies at the TiO_2 surface. This behavior provides strong evidence that the $\text{PVK}:\text{TiO}_2$ could be considered as a promising donor:acceptor system for potential fullerene-free solar cells applications.

4. Conclusions

In this report we studied the interaction between a monomer of poly (9-vinylcarbazole) and a TiO_2 surface without vacancies, with titanium and oxygen vacancy. According to the calculated adsorption energies, all surfaces presented favorable adsorptions. In both vacancies systems the molecule adsorption is more favorable than the non-vacancy surface. Upon the adsorption of the VK monomer, the Fermi level shifts close to the TiO_2 surface conduction band edge yielding to an n-type semiconducting behavior. This could be suggesting that the VK monomer is acting as an electron donor promoting the electronic doping of the TiO_2 surface. However, the presence of vacancies in the TiO_2 surface yielded interesting modifications of the electronic properties. For instance, the difference between the LUMO level of VK and the conduction band of $\text{TiO}_2\text{-O}$ surface is only ~ 0.2 eV, thus allowing to infer a decrease in the energy barrier associated to the injection of electrons from VK towards the $\text{TiO}_2\text{-O}$ surface. The charge density differences in all systems also revealed that the donor:acceptor model is plausible and concur with the previous results, suggesting promising features for potential application as donor:acceptor systems in fullerene-free solar cells.

Acknowledgments

The authors thank the Uruguayan CSIC, ANII, and PEDECIBA funding institutions.

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