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Computational exploration of charge transfer dynamics in dye sensitized SnO_2 and ZnS for photocatalytic applications

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Abstract. A computational investigation of some novel charge transfer complexes, prepared by the adsorption of dyes on SnO_2 and ZnS, was carried out using semiempirical PM3 method. Natural dyes Chlorogenic acid (DTC) and Flavone (PHC) were adsorbed on $1 \times 1 \times 1$ SnO_2 and ZnS crystals to form SnO_2-DTC, SnO_2-DTC-PHC, and ZnS-DTC adsorption complexes. The electronic absorption spectra calculated using PM3 method showed a large bathochromic shift to 958 nm and 577 nm for SnO_2-DTC and SnO_2-DTC-PHC, respectively, suggesting the charge transfer complex formation. Moreover, the bandgap was reduced to 1.29 and 2.15 eV as compared to 3.4 eV of pristine SnO_2. Subsequently, the adsorption of DTC on ZnS was accomplished and calculations were performed to determine the spectroscopic properties of the complex, where a considerable red shift was observed for ZnS-DTC as well. The semiempirical PM3 calculations pointed to stability of SnO_2-DTC, SnO-DTC-PHC, and ZnS-DTC as predicted from negative adsorption energy values. The energies of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) determined from single-point energy calculations were concomitant with the proposed photocatalytic mechanisms.

1. Introduction

Semiconductor oxides, particularly TiO_2, have been widely studied as photoactive material for numerous photocatalytic applications. The photocatalytic properties of semiconductor oxides are due to the suitable bandgap where electrons can be excited by the absorption of light creating electron-hole pairs. The photogenerated electron-hole pairs can reduce and oxidize other compounds by various mechanisms. Commonly studied semiconductor oxides include TiO_2, ZnO, CdS, WO_3, ZnS, SnO_2, NiO, etc. However, due to the higher bandgap of most of the semiconductor oxides, visible light absorption and the activity of the photocatalyst are limited. This can be compensated by sensitization of the semiconductor oxide surface with dyes that absorb in the visible region forming complex molecules that have a wide absorption spectrum [1]. Such a photocatalyst is of immense significance in the present world as a renewable energy source for numerous applications such as photocatalytic water splitting, water purification, degradation of waste dyes, photocatalytic organic transformations, and dye sensitized solar cells. In this regard, many researchers have undertaken experimental and com-

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putational research to investigate dyes that can be employed as suitable sensitizers [2,3]. A recent article has reported an artificial Z-scheme constructed using $HCa_2Nb_3O_{10}$ nanosheets sensitized by a Ru(II) tris-diimine type photosensitizer [4] employed for water splitting through the absorption of visible light. A high apparent quantum yield of 2.4% was reported at 420 nm. Another recent article explored the evolution of H_2 as a result of photocatalytic water splitting using Cu_2WS_4 nanocubes and Cu_2WSe_4 nanosheets sensitized with eosin-Y and triethanolamine [5] reporting hydrogen evolution rates of 1260 μmol/g/h and 861 μmol/g/h for two materials, respectively. Another research group investigated the photocatalytic activity of TiO_2 sensitized with Mangosteen, a natural dye, for degradation of Methylene blue [1]. The percentage of the degradation of methylene blue was studied by varying pH and catalyst amounts with the highest age degradation of 52.7% at pH 6.6 and 0.75 g/L of the photocatalyst [1]. TiO_2 sensitized with natural dye obtained from spinach has been investigated in another recent article with about 60% reduction of methylene blue over a 2-hr time horizon [6]. Recent research has explored the enhancement of H_2 evolution and molecular oxygen activation via dye sensitized $BiOBr_{0.9}\ I_{0.1}$ under visible light.

Many authors have also reported photocatalytic degradation of waste materials using dye sensitized semiconductor oxides such as TiO_2, WO_3, and ZnO [7–11]. The applications of photocatalysts are not limited to water splitting and degradation; rather, they are evaluated for their potential in water purification [12]. Bandgap engineering of semiconductor oxides using dyes as sensitizers is one of the most researched topics nowadays owing to its many applications [13–15].

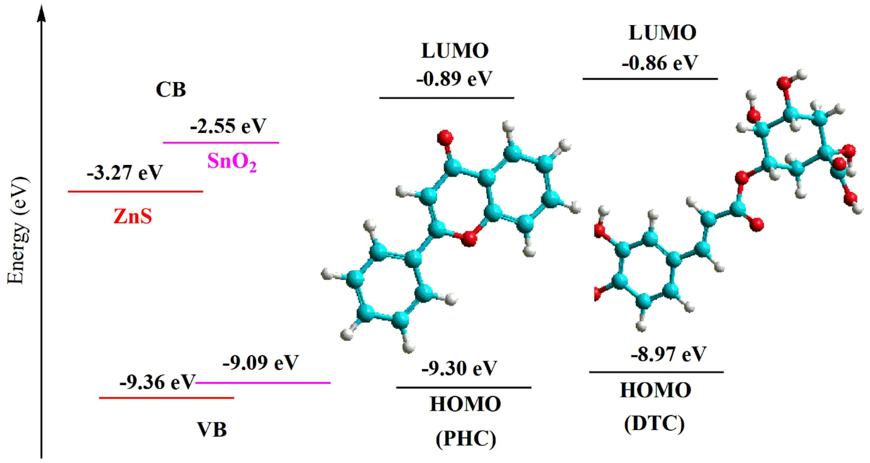
The present research is focused on the computational investigation of novel charge transfer complex prepared by the adsorption and co-adsorption of two dyes on SnO_2 and ZnS crystals, independently. The electrochemical and spectroscopic properties of the materials were predicted using semiempirical PM3 method in Hyperchem. The results demonstrated the significant enhancement of visible light absorption after dye sensitization of SnO_2 and ZnS, ensuring that the material can serve as an efficient photocatalyst for various applications. The dyes exploited for adsorption are Chlorogenic acid (DTC) and Flavone (PHC) forming *novel charge transfer* complexes with ZnS or SnO_2 that have not been reported previously to the best of our knowledge.

2. Materials and methods

Chlorogenic acid-based dye (DTC) and Flavone (PHC) were chosen for physical adsorption on SnO_2 and ZnS crystals. Semiempirical PM3 method was utilized to optimize the compounds by selecting ‘Polak Ribiere’ algorithm and RMS gradient of 0.1 kcal/ÅMol (75 maximum cycles) [16] owing to their simplicity and fast results. Single-point energy calculations were performed using PM3 method. Electronic absorption spectra were calculated through PM3 method fixing 3 occupied and 3 unoccupied electrons. Hyperchem Professional 08 was employed for all computational measurements [16].

3. Results and discussion

Computational studies were performed using chlorogenic acid (DTC) and flavone (PHC), given in Nomenclature, as their IUPAC names on SnO_2 and ZnS crystals independently. The physically adsorption (Scheme 1) was first performed independently on 1×1×1 SnO_2 crystal to form adsorption complexes represented as SnO_2-DTC and SnO_2-PHC, respectively, in the upcoming section. The key to the selection of



Scheme 1. The comparative energy level diagram of dyes and semiconductor oxides before adsorption obtained using semiempirical PM3 calculations.

dyes is their highest and lowest occupied energy values, which are determined computationally as well. As the first step of this adsorption study, the molecules were optimized and then, subjected to single-point energy calculations by selecting semiempirical PM3 method [16]. From these calculations, we obtained the total energies and E_{HOMO}/E_{LUMO} values that in turn enabled us to predict electron excitation and recombination with holes, which will be discussed in Subsection 3.1 in detail. The comparative energy level diagram of dyes and semiconductor oxides before adsorption is shown in Scheme 1.

The positions of Highest Occupied Molecular (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) orbitals are of prime importance in dye adsorption on semiconductor oxide materials. This is because upon irradiation with sunlight, the electrons in dye molecules are excited from HOMO to LUMO energy level [17]. The excited electrons in the LUMO of dye molecules can move to the Conduction Band (CB) of the semiconductor oxide if it is located below the LUMO of the dye molecules or can be utilized for reduction of chemical species [18,19]. The relative positions of HOMO/LUMO of dyes and CB/VB of semiconductor material are also of great significance to generate a strong redox potential. Lower charge recombination rates are also desired for better photocatalytic activity so that electrons in the LUMO can be utilized.

To evaluate the potential of dyes as sensitizers, electronic absorption spectra were calculated for DTC and PHC independently as well as after adsorption on SnO_2. The theoretical electronic absorption spectra of SnO_2 and DTC are displayed in Figure 1. It can be seen that λ_{max} is located at 230 for SnO_2; however, small absorption peaks were also observed at higher wavelengths, extending the absorption range to 363 nm.

DTC exhibited a group of peaks located between 190–340 nm with λ_{max} at 228 nm. Both SnO_2 and DTC seem to be absorbed in the UV region before complex formation. According to the literature, SnO_2 has an approximate bandgap of 3.6 eV [20] corresponding to 345 nm of the wavelength of light. The theoretical absorption spectrum of SnO_2 predicts the band gap of 3.4 eV, close to the literature quoted value. Adsorption of DTC dye was done on SnO_2 with the aim of improving the visible light absorption of the material. The ability of dyes to adsorb on the surface of semiconductor oxides by anchoring groups such as -OH is a well-known phenomenon, as reported in the literature [21–24]. DTC adsorption on SnO_2 was accomplished via attachment to oxygen of the -OH bond. For this purpose, H atom was removed and oxygen was bonded with Sn^{4+} of SnO_2 crystal. The resulting complex, represented as SnO_2-DTC, was subjected to single-point energy calculations after optimization to obtain the total energy of the resulting complex and HOMO/LUMO energy values (see Table 1) [16]. The energy of SnO_2-DTC complex was found to be −141407 kcal/mol. The large negative value manifests the stability of the complex between SnO_2 and DTC. Furthermore, we also determined the adsorption energy of SnO_2-DTC using the formula $E_{ads} = E_{Complex} - (E_{adsorbate} + E_{adsorbent})$ [25–27], giving a value of −408.2 kcal/mol. Again, the negative adsorption energy suggests the feasibility of the hypothetical complex between SnO_2 and DTC. The location of HOMO and LUMO (see Figure 2) manifests a charge transfer from DTC to SnO_2 forming a charge transfer complex that is also confirmed from the theoretical electronic absorption spectrum and will be discussed in the forthcoming part.

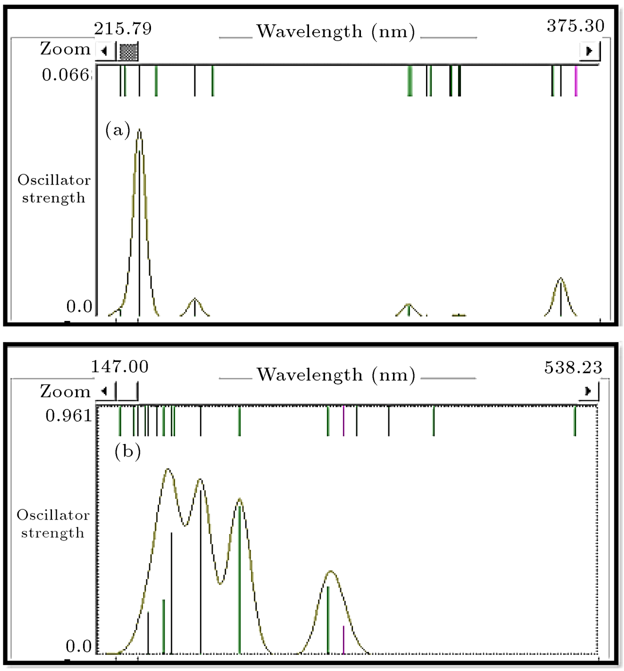


Figure 1. Calculated electronic absorption spectra of (a) SnO_2 and (b) DTC determined using semiempirical PM3 method.

We then proceed to adsorb PHC on SnO_2 along with DTC to form a co-adsorption complex designated as SnO_2-DTC-PHC. PHC was coordinated with the other Sn^{4+} of SnO_2 crystal via doubly bonded oxygen. For this purpose, the double bond of the oxygen on PHC was broken and a new bond was formed between Sn^{4+} of SnO_2 and -O of PHC.

Single-point energy calculations were performed on the co-adsorption complex to obtain the total energy and HOMO/LUMO of the co-adsorption complex. To get insight into the stability of the hypothetical co-adsorption complex, we calculated the adsorption energy of SnO_2-DTC-PHC using the previously stated formula. The adsorption energy was found to be −407

Table 1. Parameters obtained from computational calculations using semiempirical PM3 method.

Molecule	Total energy (kcal/mol)	Adsorption energy (kcal/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{max} (nm)	Spectral range (nm)
SnO_2	–30733.20	–	–9.09	–2.55	230	230–363
DTC	–111082	–	–8.97	–0.86	228	190–340
PHC	–58041	–	–9.30	–0.89	256	161–285
SnO_2-DTC	–141407	–408.2	–5.62	–2.90	350	**270–958**
SnO_2–DTC–PHC	–199449	–407.2	–5.58	–2.75	568	354–577
ZnS	–20064	–	–9.36	–3.27	347	347–644
ZnS–DTC	–130751	–395	–6.19	–2.67	400	**305–821**
ZnS–DTC–PHC	–195425	+6238	–6.50	–3.04	500	281–765

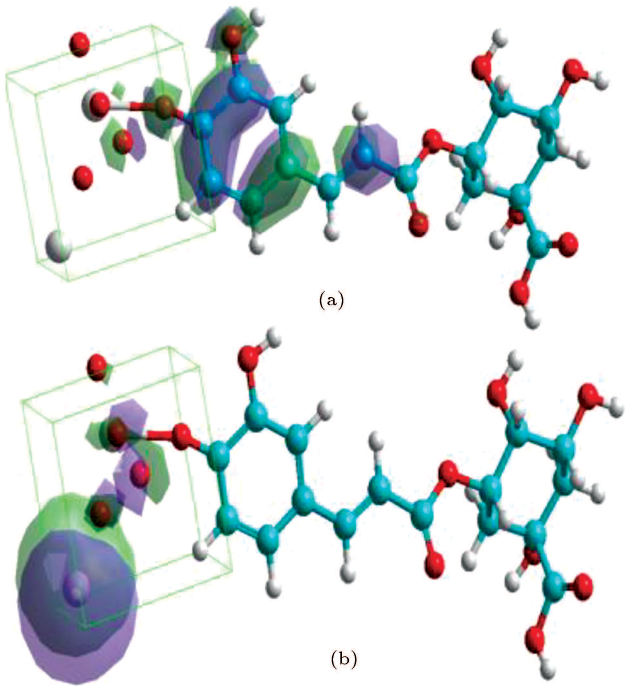


Figure 2. The representation of (a) HOMO and (b) LUMO of SnO_2-DTC.

kcal/mol, very close to SnO_2-DTC, manifesting the feasibility of the complex formation (see Table 1).

The graphical representation of HOMO/LUMO is displayed in Figure 3. It can be seen that HOMO is located on DTC, while LUMO is located partially on PHC and SnO_2, evincing that the excited electrons in DTC can provide a reduction site whereas SnO_2 and PHC can serve as the oxidation site in photocatalysis.

Furthermore, the spectroscopic properties of the adsorption complexes SnO_2-DTC and SnO_2-DTC-PHC, as displayed in Figure 4, can be compared with the absorption spectrum of pristine SnO_2 (see Figure 1(a)). It is interesting to note that the electronic absorption spectrum of SnO_2-DTC is substantially red shifted extending the absorption range up to 958 nm as compared to the absorption of pristine SnO_2 (230–363 nm). The bandgap of the hypothetical complex can also be estimated from the highest wavelength peak

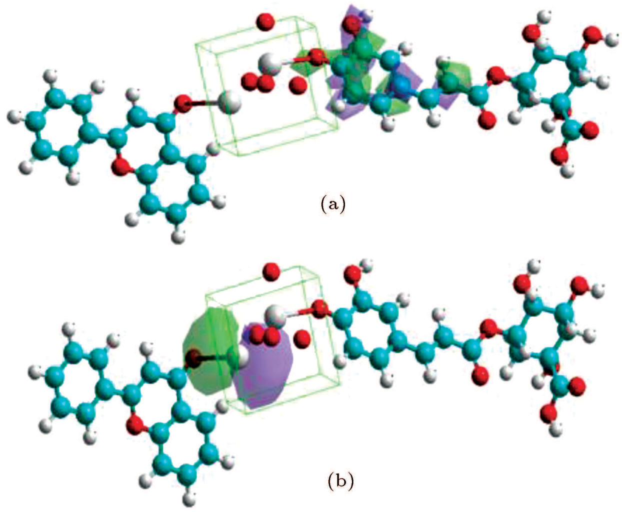


Figure 3. The graphical representation of (a) HOMO and (b) LUMO of SnO_2-DTC-PHC.

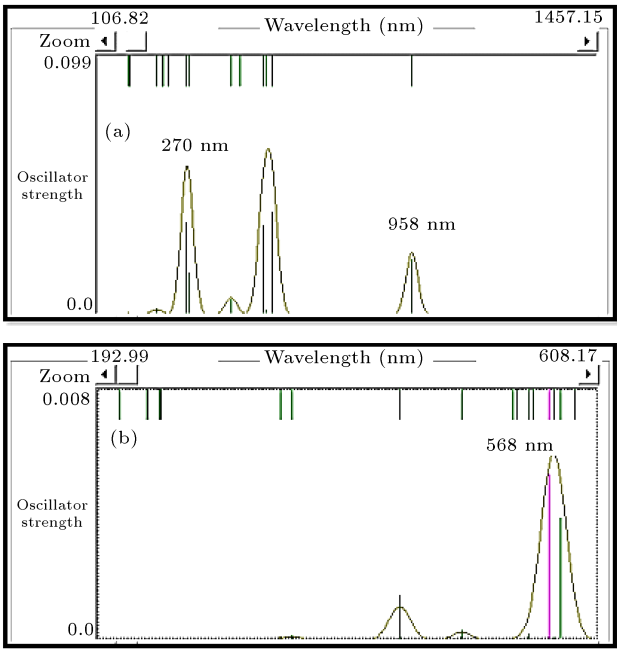


Figure 4. The calculated electronic absorption spectra of (a) SnO_2-DTC and (b) SnO_2-DTC-PHC obtained using semiempirical PM3 method.

(i.e., 958 nm) by using the relation $hc/\lambda = E$, which comes out to be 1.29 eV much lower than pristine SnO_2. It is to be noted that the optimal bandgap for dye-sensitized solar cells is reported to be 1.3 eV for maximum obtainable efficiency [28]. This suggests that SnO_2-DTC can serve as an excellent photoactive material in dye-sensitized solar cells.

The tremendous red shift suggests the formation of a strong charge transfer complex between SnO_2 and DTC [29]. The theoretical absorption spectrum of co-adsorption complex SnO_2-DTC-PHC also shows large red shift up to 577 nm. Bandgap estimation from the absorption spectrum of SnO_2-DTC-PHC shows a decline from 3.4 eV of pristine SnO_2 to 2.15 eV of the co-adsorption complex. The extension of the absorption range and bandgap reduction clearly demonstrate the high potential of the materials in photocatalytic applications such as photocatalytic degradation of waste materials, water splitting, water purification, and photocatalytic organic transformation as well as in sensitized solar cells.

Subsequently, we investigated the adsorption and co-adsorption of DTC and PHC on 1 × 1 × 1 ZnS crystal to evaluate the spectroscopic properties of the resulting complex. DTC was first adsorbed on ZnS crystal via -OH group of DTC by removing the proton and attaching it to one of the Zn atoms of the crystal. Semiempirical PM3 calculations were performed on the optimized complex to obtain the total energy and HOMO/LUMO energy values. The total energy value was employed to calculate the adsorption energy of the complex, which was found to be −395 kcal/mol, close to the adsorption energy of the earlier complexes. The negative adsorption energy indicates the feasibility of the complex formation between ZnS and DTC. The complex formed by the co-adsorption of DTC and PHC on ZnS crystal was also prepared and single-point energy calculations were performed. However, the adsorption energy for ZnS-DTC-PHC complex was found +6238 kcal/mol, pointing to the instability of the co-adsorption complex; therefore, further calculations were performed only on ZnS-DTC complex.

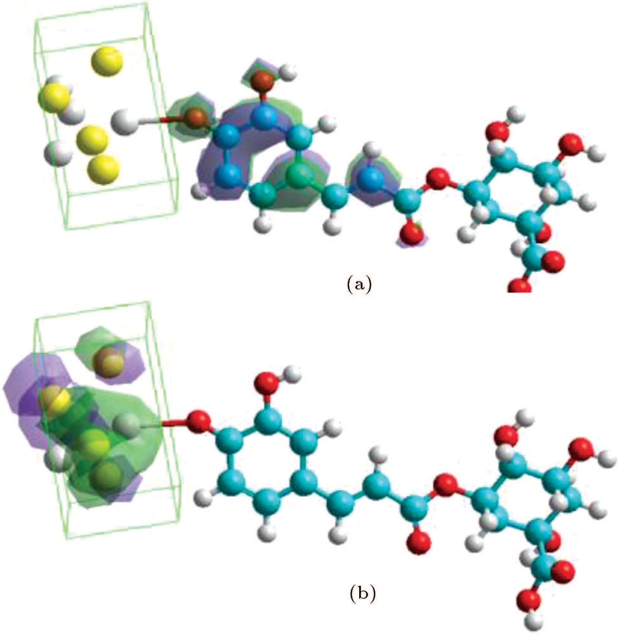
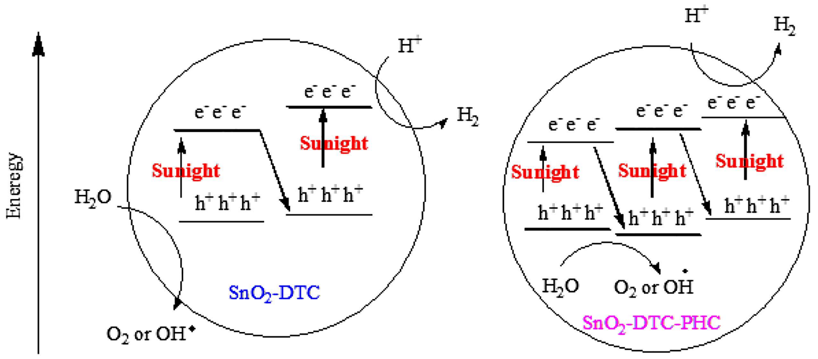


Figure 5. The representation of (a) HOMO and (b) LUMO of ZnS-DTC, suggesting electron transfer from DTC to ZnS.

The graphical representation of the HOMO and LUMO orbitals in ZnS-DTC is shown in Figure 5. HOMO is located on DTC representing probable reduction site, whereas LUMO is located on ZnS that can serve as the oxidation site in photocatalytic processes (see Scheme 2).

The theoretical electronic absorption spectrum was then calculated for pristine ZnS as well as ZnS-DTC. ZnS displayed absorption bands between 347–644 nm; however, the absorption peaks in the visible region were of very low intensity (Figure 6(a)). After adsorption of DTC, the spectrum exhibited a bathochromic shift to 821 nm with high intensity peaks in the visible range as compared to pure ZnS (see Figure 6(b)). This provided a bandgap of 1.5 eV for ZnS–DTC, making it a much suitable candidate as photoactive material in dye-sensitized solar cells.



Scheme 2. Proposed photocatalytic mechanism for SnO_2-DTC and SnO_2-DTC-PHC.

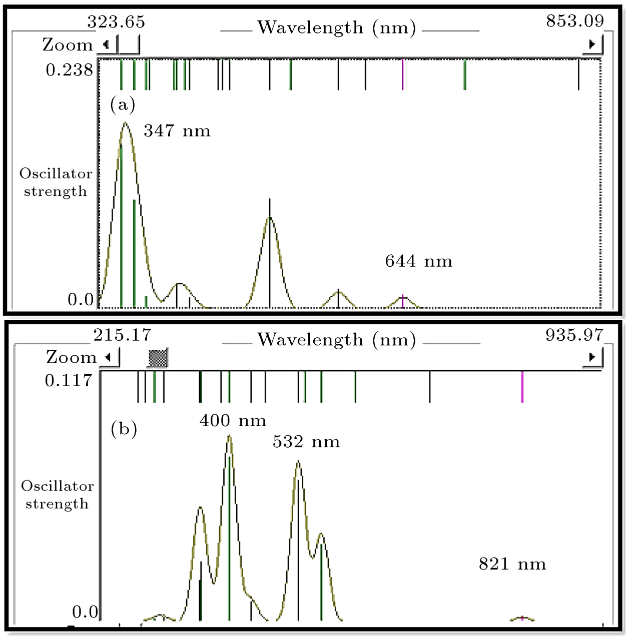


Figure 6. The calculated electronic absorption spectra of (a) ZnS and (b) ZnS-DTC obtained using semiempirical PM3 method.

3.1. Photocatalytic mechanisms

Numerous photocatalytic mechanisms shave been proposed by researchers for photocatalytic processes. Yet, we believe *s-scheme* to be most appropriate for photocatalytic processes such as water splitting and degradation of dyes. For instance, in SnO_2-DTC, electrons can be excited by absorbing UV and visible light from the LUMO to HOMO of DTC. Simultaneously, electrons can also be excited from Valence Band (VB) to CB of SnO_2 by absorbing light. As a result of this excitation, holes are created in LUMO of DTC and VB of SnO_2. The excited electrons in the HOMO of DTC can cause the reduction of the species [8]. On the other hand, the holes in VB of SnO_2 cause the oxidation process to occur. During this process, the fruitless electrons in the CB of SnO_2 can be combined with the fruitless holes in the LUMO of DTC, causing a strong redox potential [30]. Although electron transfer can take place from the LUMO of DTC to the CB of SnO_2, as proposed in other schemes, such electron transfer may not be copious due to electron-electron repulsion [8]. Moreover, for water splitting reactions to take place, the bandgap structure of the material is very important and a minimum bandgap of 1.23 eV is required [8]. According to our calculation, the bandgap of SnO_2-DTC is 1.29 eV as determined from theoretical electronic absorption spectrum; therefore, the material can serve as a photocatalyst for the water splitting process, oxidizing water to O_2 and reducing H^+ to H_2 (see Scheme 2). Photocatalytic degradation of dyes can be achieved by the generation of $OH^\bullet$ radicals from water molecules at the oxidation site of the material which can, in turn, degrade the pollutants [8].

ZnS-DTC can depict a similar photocatalytic mechanism as SnO_2-DTC. In SnO_2-DTC-PHC, electrons can be excited by UV and visible light to the HOMO/CB of the DTC, PHC, and SnO_2. The electrons in the HOMO of DTC can serve to reduce the species such as H^+, whereas the holes created in the VB of SnO_2 as well as LUMO of PHC can serve to oxidize species such as water (see Scheme 2). This is also complimented by Figure 3 where we can see the density of HOMO lying primarily on DTC and density of LUMO lying on SnO_2-PHC junction after forming the co-adsorption complex. The incorporation of PHC was done to further enhanced the absorption range; however, we have seen that SnO_2-DTC has a wider absorption range than SnO_2-DTC-PHC; therefore, the former can serve comparatively better in photocatalysis.

In addition to the photocatalytic water splitting and degradation, these materials can serve as photoactive materials in dye sensitized solar cells. The mechanism of electron production by excitation of UV and visible light is the same; however, the excited electrons travel through the external circuit and thus, generate electricity instead of being used up in reduction. SnO_2-DTC and ZnS-DTC are expected to produce good efficiency in dye sensitized solar cells owing to their large absorption range and suitable bandgap [28].

4. Conclusion

The following conclusions were drawn from the present computational study:

- The adsorption and co-adsorption of chlorogenic acid-based dye (DTC) and Flavonve (PHC) were investigated computationally on $1 \times 1 \times 1$ SnO_2 and ZnS crystal using semi-empirical PM3 method and its electrochemical and spectroscopic properties were evaluated;
- Semiempirical PM3 calculations on DTC-SnO_2 photoactive complex indicated charge transfer complex formation as evident from the theoretical electronic absorption spectrum. The spectral range was enhanced to 958 nm as compared to 363 nm of pristine SnO_2 and bandgap of SnO_2-DTC was reduced to 1.29 eV;
- The co-adsorption of DTC and PHC on SnO_2 displayed the visible light absorption up to 577 nm compared to 363 nm of pristine SnO_2 with bandgap of 2.15 eV;
- The theoretical electronic absorption spectrum of ZnS-DTC photoactive complex exhibited a bathochromic shift to 821 nm with high intensity

peaks in the visible range as compared to pure ZnS. However, ZnS-DTC-PHC complex was found to be unstable as evinced from the positive adsorption energy values;

- The escalation of the visible light absorption in SnO_2-DTC, SnO-DTC-HC, and ZnS-DTC complex suggests that they can serve as a potential photoactive material in various applications such as photocatalytic water splitting, degradation of wastes materials, photocatalytic organic transformations, and dye sensitized solar cells.

Acknowledgement

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Nomenclature

DTC	(1S,3R,4R,5R-3-(3,4-dihydroxyphenyl) acryloyloxy)-1,4,5-trihydroxycyclohexan e carboxylic acid
PHC	2-Phenyl-4H-chromen-4-one
SnO_2–DTC	DTC adsorbed on SnO_2
SnO_2–PHC	PHC adsorbed on SnO_2
SnO_2–PHC–DTC	PHC and DTC both adsorbed on SnO_2
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

References

1. Ghosh, M., Chowdhury, P., and Ray, A.K. "Photocatalytic activity of aeroxide TiO_2 sensitized by natural dye extracted from mangosteen peel", *Catalysts*, **10**(8), p. 917 (2020).
2. Takeshita, T. "Computational study of cresyl violet covalently attached to the silane coupling agents: application to TiO_2-based photocatalysts and dye-sensitized solar cells", *Nanomaterials*, **10**(10), p. 1958 (2020).
3. Sappati, S., George, L., Swamy, V.P., et al. "Descriptors to predict dye-sensitized semiconductor based photocatalyst for hydrogen evolution reaction", *ChemCatChem*, **11**(24), pp. 6460–6466 (2019).
4. Oshima, T., Nishioka, S., Kikuchi, Y., et al. "An artificial Z-scheme constructed from dye-sensitized metal oxide nanosheets for visible light-driven overall water splitting", *J. Am. Chem. Soc.*, **142**(18), pp. 8412–8420 (2020).
5. Genc, E., Coskun, H., Yanalak, G., et al. "Dye-sensitized photocatalytic hydrogen evolution by using copper-based ternary refractory metal chalcogenides", *Int. J. Hydrog. Energy*, **45**(32), pp. 15915–15923 (2020).
6. Samuel, J.J. and Yam, F. "Photocatalytic degradation of methylene blue under visible light by dye sensitized titania", *Mater. Res. Express*, **7**(1), p. 015051 (2020).
7. Kumar, S.G. and Rao, K.K. "Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO_2, WO_3 and ZnO)", *Appl. Surf. Sci.*, **391**(B), pp. 124–148 (2017).
8. Kumar, S., Kumar, A., Kumar, A., et al. "Nanoscale zinc oxide based heterojunctions as visible light active photocatalysts for hydrogen energy and environmental remediation", *Catal. Rev*, **62**(3), pp. 346–405 (2020).
9. Nimpoeno, W.A., Lintang, H.O., and Yuliati, L. "Methyl red dye-sensitized zinc oxide as photocatalyst for phenol degradation under visible light", *AIP Conf. Proc., American Institute of Physics*, US, p. 020048 (2020).
10. Esmaili, Z., Nazar, A.S., and Farhadian, M. "Degradation of furfural in contaminated water by titanium and iron oxide nanophotocatalysts based on the natural zeolite (clinoptilolite)", *Sci. Iran.*, **24**(3), pp. 1221–1229 (2017).
11. Rahim, S., Ghamsari, M.S., and Radiman, S. "Surface modification of titanium oxide nanocrystals with PEG", *Sci. Iran.*, **19**(3), pp. 948–953 (2012).
12. Han, Z., Fei, J., Li, J., et al. "Enhanced dye-sensitized photocatalysis for water purification by an alveoli-like bilayer Janus membrane", *Chem. Eng. J.*, **407**, p. 127214 (2021).
13. Karthikeyan, C., Arunachalam, P., Ramachandran, K., et al. "Recent advances in semiconductor metal oxides with enhanced methods for solar photocatalytic applications", *J. Alloys Compd.*, **828**, p. 154281 (2020).
14. Tahir, M., Tasleem, S., and Tahir, B. "Recent development in band engineering of binary semiconductor materials for solar driven photocatalytic hydrogen production", *Int. J. Hydrog. Energy*, **45**(32), pp. 15985–16038 (2020).
15. Gaidi, M., Daoudi, K., Columbus, S., et al. "Enhanced photocatalytic activities of silicon nanowires/graphene oxide nanocomposite: Effect of etching parameters", *J. Environ. Sci.*, **101**, pp. 123–134 (2021).
16. Munir, S., Khan, B., Abdullah, A., et al. "Computational investigations of a novel charge transfer complex for potential application in dye-sensitized solar cells", *Iran. J. Chem. Chem. Eng.*, **39**(6), pp. 19–27 (2020).
17. Maurya, I.C., Singh, S., Srivastava, P., et al. "Natural dye extract from Cassia fistula and its application in dye-sensitized solar cell: Experimental and density functional theory studies", *Opt. Mater.*, **90**, pp. 273–280 (2019).

18. Beni, A.S., Zarandi, M., Hosseinzadeh, B., et al. "Density functional theory study of carbazole dyes: Potential application of carbazole dyes in dye-sensitized solar cells", *J. Mol. Struct.*, **1164**, pp. 155–163 (2018).

19. AL-Temimei F.A. and Alkhayatt, A.H.O. "A DFT/TD-DFT investigation on the efficiency of new dyes based on ethyl red dye as a dye-sensitized solar cell light-absorbing material", *Optik*, **208**, p. 163920 (2020).

20. Sarangi, S., Pradhan, G.K., and Samal, D. "Bandgap engineering in SnO_2 by Pb doping", *J. Alloys Compd.*, **762**, pp. 16–20 (2018).

21. Ndiaye, A., Dioum, A., Oprea, C.I., et al. "A combined experimental and computational study of chrysanthemin as a pigment for dye-sensitized solar cells", *Molecules*, **26**(1), p. 225 (2021).

22. Cai, Z., Sun, Y., Liu, W., et al. "An overview of nanomaterials applied for removing dyes from wastewater", *Environ. Sci. Pollut. Res.*, **24**(19), pp. 15882–15904 (2017).

23. Ferrere, S., Zaban, A., and Gregg, B.A. "Dye sensitization of nanocrystalline tin oxide by perylene derivatives", *J. Phys. Chem. B.*, **101**(23), pp. 4490–4493 (1997).

24. Oprea, C.I., Panait, P., Lungu, J., et al. "DFT study of binding and electron transfer from a metal-free dye with carboxyl, hydroxyl, and sulfonic anchors to a titanium dioxide nanocluster", *Int. J. Photoenergy*, **2013**, p. 893850 (2013).

25. Wei, X., Dong, C., Chen, Z., et al. "A DFT study of the adsorption of O_2 and H_2O on Al (111) surfaces", *RSC Advances*, **6**(61), pp. 56303–56312 (2016).

26. Abbasi, A. "Adsorption of phenol, hydrazine and thiophene on stanene monolayers: a computational investigation", *Synt. Met.*, **247**, pp. 26–36 (2019).

27. Gómez, E.d.V., Amaya-Roncancio, S., Avalle, L.B., et al. "DFT study of adsorption and diffusion of atomic hydrogen on metal surfaces", *Appl. Surf. Sci.*, **420,** pp. 1–8 (2017).

28. Boschloo, G. "Improving the performance of dye-sensitized solar cells", *Front. Chem.*, **7**, p. 77 (2019).

29. Munir, S., Shah, S.M., Hussain, H., et al. "Adsorption of porphyrin and carminic acid on TiO_2 nanoparticles: A photo-active nano-hybrid material for hybrid bulk heterojunction solar cells", *J. Photochem. Photobiol. B*, **153**, pp. 397–404 (2015).

30. Xu, Q., Zhang, L., Cheng, B., et al. "S-scheme heterojunction photocatalyst", *Chem*, **6**(7), pp. 1543–1559 (2020).

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