JSER

Journal of Solar Energy Research (JSER)

Journal homepage: www.jser.ut.ac.ir

Vitaminized Dye-sensitized Solar Cell

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ARTICLE INFO

Received: 28 Aug 2018
Received in revised form: 25 Oct 2018
Accepted: 05 Dec 2018
Available online: 05 Dec 2018

Keywords:
Dye-sensitized solar cell; Nanomaterial; Semiconductor; Cyanocobalamin; Density functional theory; B3LYP

A B S T R A C T

Gaining solar energy by the valence electrons of the dye molecules is the first motive force to rule a dye-sensitized solar cell (DSC). This admits the importance of the dye molecule and its features, from the electronic states till the absorbance and the functional groups, to anchor to the nanostructured semiconductor photoanode, attain solar energy and finally convert it into electricity. To this purpose, the current study introduces cyanocobalamin (B12 vitamin) to play this role in DSCs. From one side, density functional theory (DFT) reveals the energy of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the bandgap of B12 vitamin as -7.4, -4.9, and 2.5 eV, respectively. On the other side, the experimental ultraviolet-visible (UV-Vis) spectroscopy on B12 solution represents its broad absorption spectrum in this region. These results show that the proposing dye perfectly matches the electronic domino of the DSC device. Furthermore, this study discloses the matching semiconductors, redox shuttles, and counter electrodes (CEs) to construct B12-vitaminized dye-sensitized solar cells.

1. Introduction

The photovoltaic devices, which they directly convert the solar energy into available electricity are based on the charge-separation process at the interface of two materials with distinguished conduction mechanisms [1]. Numerous devices were already developed which classified as four different generations of solar cells [2]. Here, we have focused on a low-cost and environmentally-friendly device from the third generation of the solar cells, so-called dye-sensitized solar cell (DSC). This photoelectrochemical device comprises three main components; a dye-sensitized mesoporous nanocrystalline semiconductor photoanode, a counter electrode (CE) and a redox electrolyte [3]. Sensitization of photoanodes is usually possible using organic/inorganic molecules, quantum dots, polymers, etc, the component that absorbs the solar light and begins the charge-transfer process through the charge-separation root [1,4]. Briefly, after the photo-excitation of the dye molecules through light absorption, the injection of the photoelectrons into the conduction band (CB) of the semiconductor takes place. In following, the oxidized dye molecules are regenerated by means of the electron donation from the redox couple in the electrolyte; usually I^-/I_3^- or Co^{2+}/Co^{3+}. Finally, the reduction of the oxidized electrolyte component occurs at the counter electrode and permits the reversible device operation. It can be seen that the power-generation process would never work properly unless it employs a suitable initiator, *e.g.* a dye molecule. There are some criterions to employ an ideal sensitizer in the DSC [1], like:

- Broad absorption coverage from ultraviolet (UV) till near infrared (NIR) regions with high absorption coefficients,
- Containing functional groups to anchor to the semiconductor layer, and
- Electronically matching with the energy levels of the other components in the cell.

Thus, various attempts have been done to introduce or prepare sensitizers, especially dyes, fulfilling these terms [3,5-7]. Generally, ruthenium-based complexes have been used to sensitize photoanodes in DSCs [8]. However, these dyes are very expensive and hard to prepare. Therefore, determining an alternative, low-cost and green compound with similar characteristics is of great importance. Natural compounds like pomegranate juice, as well as coumarin, indoline, and merocyanine, were studied as replacements for ruthenium dyes [9-11]. In order to save time, money, and energy, the computational calculations become valuable in determining the structure and features of different compounds, potentially matching the solar cell criterions. Density functional theory (DFT) is a convenient method widely used to study the structure and the energy levels of different dye molecules [12-14].

In this study, we have focused on modeling a green dye, cyanocobalamine (B12 vitamin), using density functional theory. In addition, its applicability in DSCs was estimated, reviewing the electronic levels of the other components, i.e. semiconductors, redox couples and counter electrodes, which suggests the possible appropriate materials for preparing a B12-vitaminized DSC. To the best of our knowledge, there is no report on the exploitation of B12 in solar cells.

2. Materials and Methods

2.1. Computational calculations

All modelings and computational calculations were performed using the DFT-B3LYP method with 6-31G* basis set in Wavefunction Spartan 16' package [15].

2.2. Materials

Cyanocobalamin ampuls, produced by the Exir Pharmaceutical Co. were purchased from a local pharmacy and diluted in ethanol (99.99%, Merck) for further study.

2.3. Instrument

The Agilent 8453 ultraviolet-visible (UV-Vis) spectrophotometer was used to determine the absorption spectrum of the B12 ethanol solution.

3. Results & Discussion

Figure 1 represents the optimized model structure of cyanocobalamin ($C_{63}H_{88}CoN_{14}O_{14}P$) with the calculated orbital energy diagram using DFT/B3LYP/6-31G* method. The average bond lengths were measured as: Co-N (1.940 Å), C≡N (1.167 Å), C=N (1.326 Å), C-N (1.394 Å), P=O (1.503 Å), P-O (1.608 Å), C=O (1.233 Å), C-O (1.429 Å), C=C (1.396 Å), C-C (1.529 Å), N-H (1.011 Å), O-H (0.970 Å), and C-H (1.092 Å).

As it is depicted in the energy diagrams of Figure 1, there are two types of HOMO and LUMO orbitals dedicated to the B12 molecule. The orbital and bandgap energy values are as: -7.4 (E_{aHOMO}), -4.9 (E_{aLUMO}), 2.5 ($\Delta E_{aHOMO-aLUMO}$), -7.4 (E_{bHOMO}), -6.7 (E_{bLUMO}), and 0.7 ($\Delta E_{bHOMO-bLUMO}$) in eV unit. Therefore two types of photoelectron transition would occur in this molecule. The low value of bandgaps (< 2.5 eV) gives the favorable property to the vitamin to absorb light energy in the ultraviolet and especially visible region. This property is highly crucial for a compound to take the sensitizer role in the DSC device performance.

In order to have the further understanding about the property of the B12 compound, its solution in ethanol was subjected to the UV-Vis spectroscopy. Figure 2 displays the typical [16] broad absorption spectrum of cyanocobalamin in the wavelength range of 230-630 nm, which perfectly matches the solar radiation spectrum in the mentioned region. This may also guaranty its applicability as a sensitizer in DSC devices. Since the broader absorption spectrum comes from the absorption of more photons, it would result in the higher amount of photo-excited electrons and therefore better device performance.

This study shows that B12 is potentially favorable to act as a sensitizer in DSCs, however, fabricating solar cells comprising of the components matched with B12 is a great challenge. In the beginning, defining a suitable photoanode is crucial according to the electronic properties. The energy values of the molecular orbitals dedicated to the different semiconductors potentially able to be used as photoanodes in DSCs were published elsewhere [17-29].

As the bandgap value of B12 was found to be 2.5 eV, it is more convincible to choose a photoanode material with the higher bandgap value (i.e. >2.5 eV). Table 1 represents a list of these semiconductors in the order of band gap widening. At first glance, the semiconductors above the threshold of 2.5 eV bandgap (in Table 1) might be favorable to be sensitized by B12.

However, the other determining rule on the mechanism of DSCs performance is that the LUMO of the sensitizer must be higher than the LUMO of the semiconductor in the energy diagram [4].

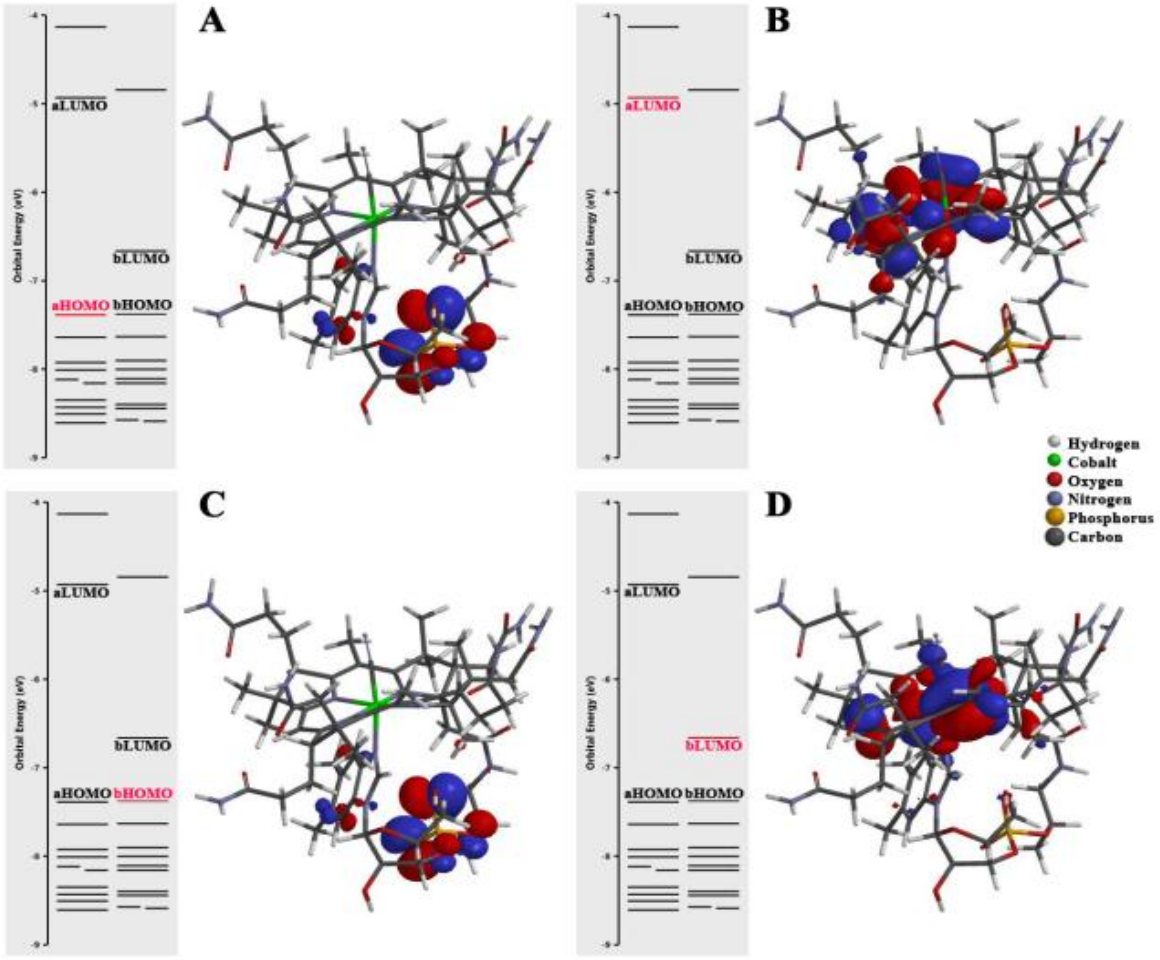

Figure 1. The structure and the orbital energy values of (A) aHOMO, (B) aLUMO, (C) bHOMO, and (D) bLUMO of the B12 vitamin.

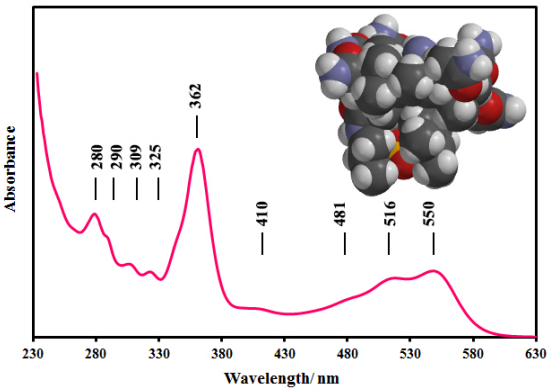

Figure 2. The UV-Vis spectrum of B12 vitamin (Inset: the space filling structure).

Therefore the mentioned list would be shrunken to match with the B12 vitamin. Considering these two conditions, we suggest MnO_2, WO_3, CoO, Bi_2O_3, and SnO_2 as potentially suitable compounds to construct B12-vitaminized photoanodes.

Similarly, we reviewed the redox compounds able to donate and accept electrons between the two electrodes in the DSC structure [30,31]. Table 2 discloses the electronic state of some redox couples used in DSCs. Generally, the redox couples whose HOMO energy levels stand between the HOMO and the LUMO energy levels of the dye molecules, are potentially able to regenerate the oxidized dyes. Considering the energy levels of B12 and the list in Table 2, one may come to the conclusion that conventional I^-/I_3^- and T^-/T_2 couples do not match with this sensitizer, however, the Co^{2+}/Co^{3+}-based electrolytes as well as Fc/Fc^+ and S^{2-}/S_n^{2-} might be favorable to act as redox shuttles in B12-sensitized solar cells.

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Table 1. The bandgap energy values of different semiconductors.

N	Material	$\Delta E_{HOMO-LUMO}$ (eV)
1	MnO_2	2.5
2	ZnSe	2.7
3	WO_3	2.7
4	V_2O_5	2.8
5	$PbTiO_3$	2.8
6	CoO	2.8
7	In_2O_3	2.8
8	Bi_2WO_6	2.8
9	PbO	2.8
10	$FeTiO_3$	2.8
11	Bi_2O_3	2.9
12	TiO_2 (rutile)	3.0
13	$CuTiO_3$	3.0
14	MoO_3	3.0
15	$MnTiO_3$	3.1
16	TiO_2 (anatase)	3.2
17	ZnO	3.2
18	ZnS	3.4
19	GaN	3.5
20	$KTaO_3$	3.5
21	$CaTiO_3$	3.5
22	NiO	3.5
23	MnO	3.6
24	SnO_2	3.8
25	Ge_3N_4	3.8
26	Ta_2O_5	4.0
27	ZrO_2	5.0

Table 2. The HOMO energy values of different redox couples.

N	Material	E_{HOMO} (eV)
1	I^-/I_3^-	-4.89
2	T^-/T_2	-4.89
3	$[Co(terpy)_2]^{2+/3+}$	-4.94
4	$[Co(bpy)_3]^{2+/3+}$	-5.01
5	$[Co(phen)_3]^{2+/3+}$	-5.04
6	Fc/Fc^+	-5.06
7	$[Co(dbbip)_2]^{2+/3+}$	-5.07
8	$[Co(dmbip)_2]^{2+/3+}$	-5.13
9	$[Co(Cl\text{-}phen)_3]^{2+/3+}$	-5.16
10	$[Co(NO_2\text{-}Phen)_3]^{2+/3+}$	-5.29
11	$[Co(bpy\text{-}pz)_3]^{2+/3+}$	-5. 30
12	S^{2-}/S_n^{2-}	-5. 49

Generally, the reduction reactions of the shuttle components take place at the surface of CE whereas the oxidation occurs at the surface of the photoanode, making the dye regeneration possible. Therefore, the circuit of the DSC is completed using a compatible counter electrode, e.g. Pt or carbon-based materials, which, facilitate the reduction reaction of the mentioned redox species [3,32-34]. This report reveals that the B12 vitamin is potentially applicable to be used as sensitizers in DSCs, considering the electronic properties of other components. However, the authors declare that despite all these theoretical investigations, further electrochemical studies are needed to fabricate a B12-sensitized solar cell with reasonable efficiency.

4. Conclusions

This report is the first demonstration on the electronic applicability of cyanocobalamin to act as a sensitizer in dye-sensitized solar cells. To this purpose, DFT calculation was employed to determine the molecular orbital energy levels of this vitamin, which perfectly matches the basic principles of the DSC structure. Furthermore, the UV-Vis light absorption spectroscopy represents the broad absorption area, dedicated to B12, to capture the most incoming light as the first key role in the performance of the solar cells. In addition, our mini revision on the electronic features of other components come to suggest potentially suitable semiconductor photoanodes, redox couples, and counter electrodes, constructing convenient DSCs. In fact, further electrochemical studies would reveal that which components perform the highest power-conversion efficiency for the vitaminized solar cell.

Acknowledgements

The authors would like to thank Razi University of Kermanshah.

i) Nomenclature
ii) B12 Cyanocobalamin

bpy	2,2'-bipyridine
bpy-pz	6-(1H-pyrazol-1-yl)-2,2'-bipyridine
CB	Conduction band
CE	Counter electrode
dbbip	2,6-bis(1'-n-butylbenzimidazol-2'-yl)pyridine
DFT	Density functional theory
dmbip	2,6-bis(1'-methylbenzimidazol-2'-yl)pyridine
DSC	Dye-sensitized solar cell
Fc	Ferrocene
Fc^+	Ferrocenium
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
NIR	Near infrared
phen	1,10-phenanthroline
T^-	5-mercapto-1-methyltetrazole ion
terpy	2,2':6',2''-terpyridine
UV	Ultraviolet
Vis	Visible

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