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DFT electron transport study of quantum dot sensitized solar cells linkers

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ABSTRACT

In this paper, electron transport in quantum dot sensitized solar cell (QDSSCs) linkers is studied by using density function theory (DFT). Experimentally, the linker effect on the solar cell efficiency has been a topic of interest to researchers. However, electron transport in linkers is simulated in this paper for the first time. We have introduced a new figure of merit as "molecular resistance parameter" to compare the performance of the linkers. In this study, 3-Aminopropyl trimethoxysilane (APS), p-Aminophenyl trimethoxysilane (APhS), Mercaptobenzoic acid (MBA), Mercaptopropionic acid (MPA) and Mercaptoacetic acid (MAA) Molecules are simulated as common linkers in quantum dot sensitized solar cells. In addition, we compared electron transport for APS and APhS linkers in case of three atoms of linker interact with the electron acceptor and case of only one atom of linker interact with the electron acceptor. In this study, DMol3 is used to simulate the optical and electrical properties of linker molecules. The simulation results can be used in the optimization of quantum dots sensitized solar cells.

1. Introduction

The initial design of quantum dot sensitized solar cells (QDSSCs) has been inspired by dye-sensitized solar cells (DSSCs) [1]. In QDSSCs, the excited pairs of electron and hole are formed by photon absorption in quantum dots. Then, the electrons eject from quantum dot (QD) to electron acceptor and the holes eject from QD to hole transporting material (HTM). The Separation of excited electrons and holes reduce the recombination rate in QDSSCs. Absorption of QD on the surface of electron acceptor is done by using direct adsorption methods [2,3] or adsorption via a linker [4,5]. QDSSCs parts in the case of using linker are shown in Fig. 1. As shown in Fig. 1 linkers molecules on the one hand are absorbed by QD and on the other hand are absorbed by electron acceptor. The transmission of exited electron from QD to electron acceptor is the role of linker's molecule in QDSSCs.

Experimental study of the linker effect on the solar cell efficiency has been a topic of interest to researchers [4,6,7]. Density function (DFT) theory is a widely used method to simulate the organic compounds properties [8–10]. DFT simulation the optical and electrical properties of DSSC linkers has been studied previously [11–13]. However, electron transport in linkers is simulated in this paper for the first time. The optical and electrical properties of QDSSCs linkers is also studied. In addition, we propose molecular resistance parameter in other to compare the difficulty to pass electrons through linker

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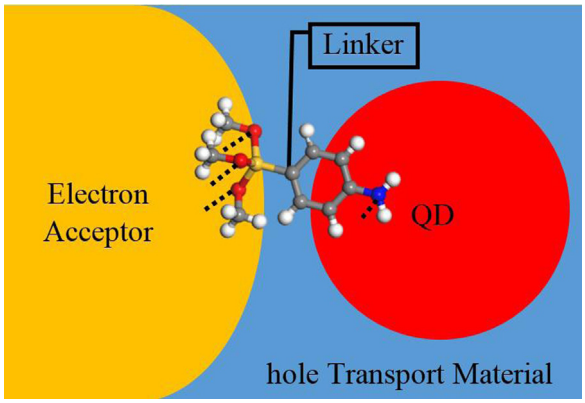

Fig. 1. Schematic representation of the quantum dot sensitized solar cell main parts.

Table 1
List of simulation parameters.

Parameter	Value	
Functional	GGA-PBE	
Maximum energy change	10^{-5} Ha/atom	
Maximum force	0.002	
Maximum stress	0.2 GPa	
SCF tolerance	10^{-6} Ha/atom	
Max grid Poisson solver	0.2 Å	
Basis set	DNP	
Basis file	4.4	
Orbital cut	Nitrogen compounds	4.6 Å
off	Sulfur compounds	4.0 Å
Electronic minimizer	All Band/EDFT	

Ha = Hartree energy = 27.211396132 eV.

molecules. In other word, molecular resistance can be used to compare the performance of linkers. Simulated linkers in this paper are: 3-Aminopropyl trimethoxysilane (APS), p-Aminophenyl trimethoxysilane (APhS), Mercaptobenzoic acid (MBA), Mercaptopropionic acid (MPA) and Mercaptoacetic acid (MAA). Practically, the APhS and APS can be absorbed on the electron acceptor by different surface interactions [14]. In one case, two oxygen atoms of linkers are shared with the Neighboring molecules, and one oxygen atom have interaction with the electron acceptor surface. In other case, all oxygen atoms of linker's molecule are interacted with the electron acceptor surface. The simulated linkers in this study are the most common linkers in QDSSCs.

Various materials can be used in QDSSCs as the electron acceptor (e.g. ZnO and TiO_2) and the quantum dot (e.g. CdSe, CdS, CdTe, PbS, PbSe). Therefore, the effect of the exited electrons transfer from QD atom to linker and the effect of electron transfer from the linker to electron acceptor is ignored in this study. The electron injection from quantum dots to linkers and from linker's molecules to electron acceptor can be the subject of future research. In the simulation section of this study, the simulated linker's structures and the simulation parameters are expressed. In the results and discussion section, the current–voltage curves, density of states and the HOMO and LUMO orbitals are studied as the electrical properties of linkers. In addition, absorption spectrum of linkers is studied as most important parameter in optical properties of linkers.

2. Simulation

Fig. 2 shows the molecular structure of the simulated linkers and those electrodes. In the simulated linkers Nitrogen (N) or sulfur (S) atoms are interacts with the quantum dot and oxygen atoms are interacts with the electron acceptor. Electrode location in simulated linkers is inspired by electrons flow in real linkers. Electrode locations are as follows: First electrode is selected N or S atoms and the second electrode is selected oxygen atoms. Actually, in APS and APhS linkers there is a probability that the electron acceptor absorb only one oxygen atom of linker. Therefore, in APS and APhS linker's simulation in the one case, electrode is selected one oxygen atom of linker and in the other case, electrode is selected three oxygen atoms of linker. In this study, GAA-PBE functional [15] is used in geometry optimization and properties simulation. GGA is widely used functional which has been proved an efficient approach to reproduce the experimental data. Moreover, various electronic, optical and charge transfer properties were studied where it was proved that PBE functional is rational [16,17]. Simulation parameters are shown in Table 1. In this paper, DMol3 software from Material Studio package is used in simulations.

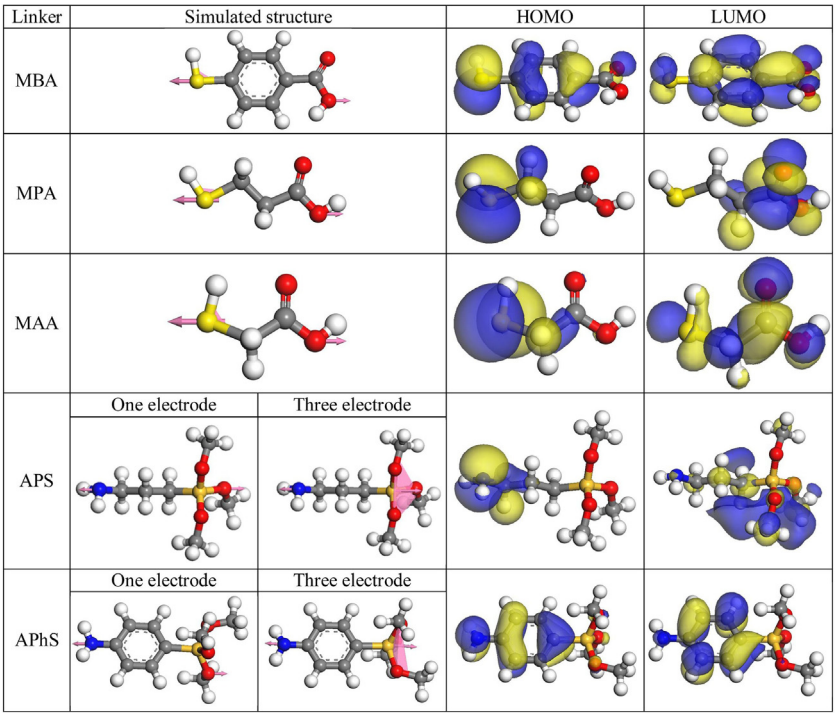

Fig. 2. molecular structure of the simulated linkers and those electrodes.

Table 2
The calculated HOMO and LUMO energy of the simulated linkers.

Linkers	HOMO Energy	LUMO Energy
MBA	−5.879 eV	−2.501 eV
MPA	−5.595 eV	−1.298 eV
MAA	−5.726 eV	−1.578 eV
APS	−5.384 eV	0.431 eV
APhS	−5.131 eV	−1.079 eV

3. Results and discussion

Fig. 2 shows the calculated HOMO and LUMO orbitals in the simulated linkers. The LUMO orbitals position in linkers is very important because the role of linkers is transfer of exited electrons. As shown in Fig. 2, LUMO orbitals position in the simulated linkers, expect MPA are acceptable to transport electrons. The linkers of MBA and MAA have the most appropriate orbitals position in other to transfer electrons from quantum dot to electron acceptor. HOMO and LUMO energy levels and the density of states are important parameters in the choice of QDSSCs linkers. Fig. 3 shows the calculated density of states for the linkers of MBA, MPA, MAA, APS and APhS. In Fig. 2, HOMO energy is considered as a reference (zero energy). The exact amount of the HOMO and LUMO energy is shown in Table 2. Fig. 4 shows the calculated absorption spectrum of simulated linkers. As shown in Fig. 4, Absorption in the likers of MBA, MPA and MAA is less than Absorption in the linkers of APS and APhS. In any case, the pick position of absorption in all of the simulated linkers is in the range of low intensity solar radiation. This means that the masking effect of linkers on the reducing the quantum dots absorption energy is very low.

Fig. 5a–c shows the current–voltage curve for the linkers of MBA, MPA and MAA, respectively. According to Fig. 5a–c, it can be said that reduce the linkers current by the increasing length of string or carbon structure between sulfur atom and oxygen atoms. However, reduce current by the increasing length of linker was predictable by classical physics. The curves are approximated by a set of linear curve for a more detailed study. In each section of current–voltage curves, the curve slope and the resistance relationship is reversed. The Characteristic curves slope in the range of 0.9–1.2 V is less than the Characteristic curves slope in the range of 0–0.9 V for the linkers of MPA and MAA. Accordingly, the best voltage range to optimization performance of the MAA and MPA is less than 0.9 V. In addition, MBA characteristic curve shows that the best voltage to optimization performance of MBA is about 1.2 V. Fig. 5d and e also shows the simulated current–voltage curves for the linkers of APS and APhS, respectively. Comparing the characteristics of APS and APhS in case of one oxygen atom as electrode shows that the resistance increase and the current Decrease by increasing the length of carbon structure in the linkers of APS and APhS such as the linkers of MBA, MPA and MAA. But Comparing the characteristics of APS and APhS with

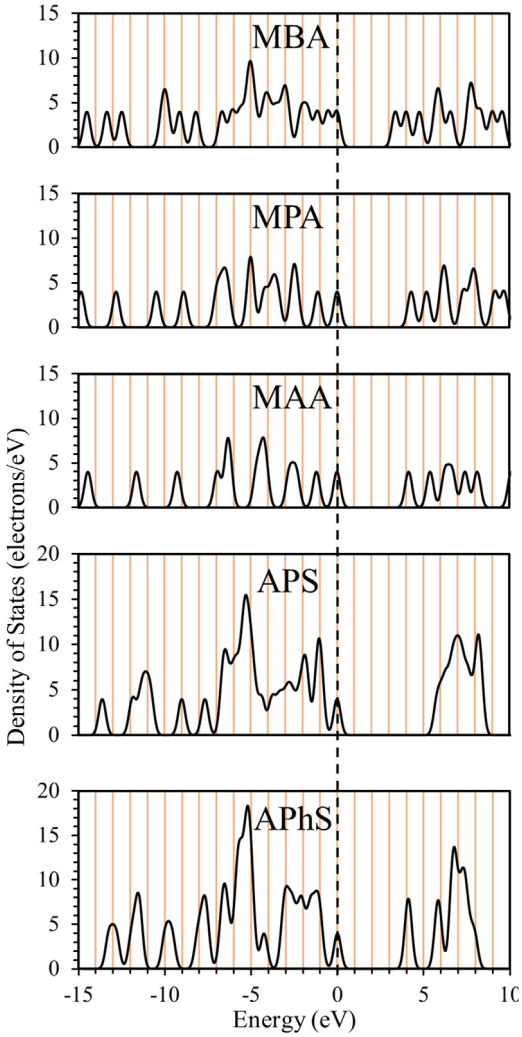

Fig. 3. The simulated density of state for the linkers of MBA, MPA, MAA, APS and APhS.

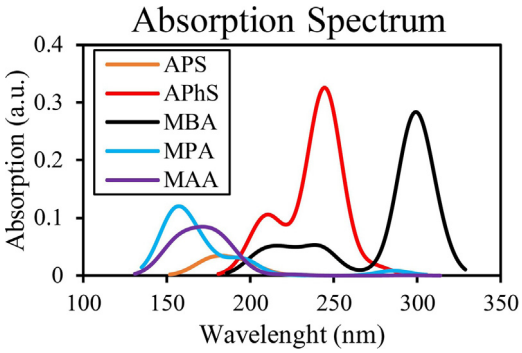

Fig. 4. Absorption spectrum for the linkers of MBA, MPA, MAA, APS and APhS.

one and three oxygen atom as electrode shows that in the case of three oxygen atoms as electrode the increasing of APhS curve slope (decreases resistance) is much more than the increasing of APS curve slope. This could be due to the aromatic rings capacity to transfer electrons and inability to use the all of these capabilities in the case of selected one oxygen atom as electrode.

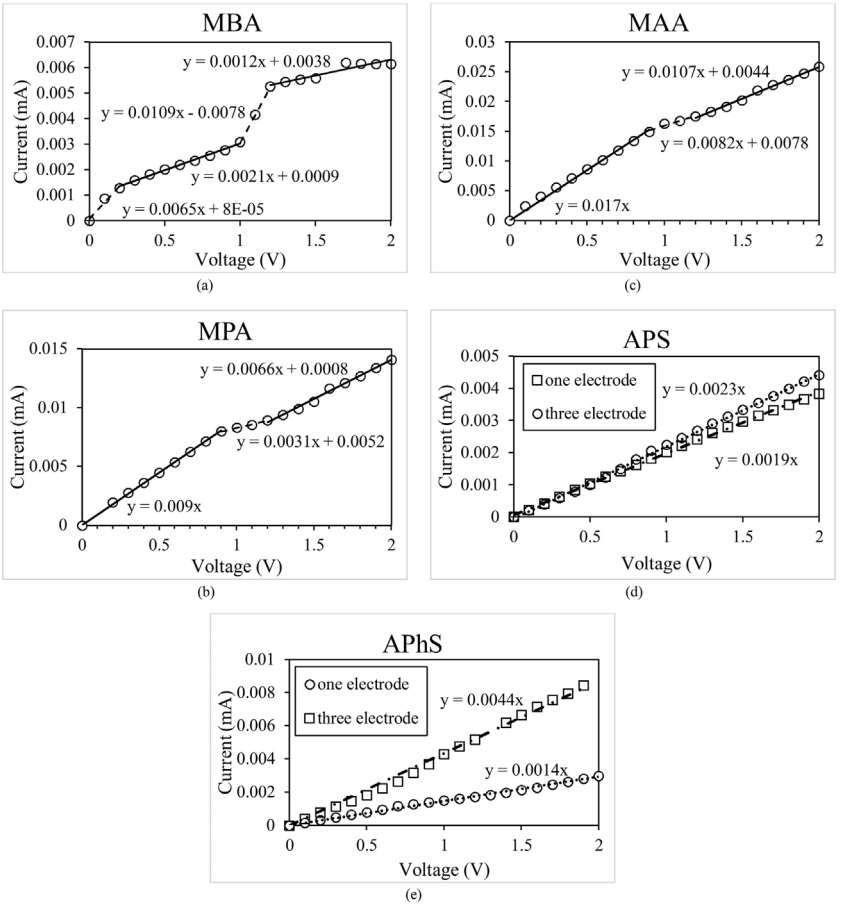

Fig. 5. The simulated current–voltage curve and the fitted linear curves for the linkers of (a) MBA, (b) MPA, (c) MAA, (d) APS and (e) APhS.

4. Conclusion

In this study, we showed that the best voltage range to optimization performance of MAA and MPA is less than 0.9 V and the best voltage to optimization performance of MBA is about 1.2 V. In APhS linker, the three of oxygen atom must be absorbed on the electron acceptor surface in other to using the electron transfer capacity of aromatic ring. In this study, the effect of electron injection from quantum dot to linker and from the electron acceptor to linker was ignored. The interaction between various quantum dots, linkers and various electron acceptors can be the subject of future research.

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