Density Functional Theory Study for Azo Dye Doped with (Si, Ti, S, Zn, Al, Cu, Ni) Atoms as A sensitizer of Dye-Sensitized Solar Cells (DSSCs)

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Abstract

The possibility of nanostructures of azo dye-doped with (Si, Ti, S, Zn, Al, Cu, Ni) atoms as a sensitizer of DSSC is investigated. The density functional theory DFT with B3LYP/6-31G is used to get the geometrical optimizations and electronic properties of nanostructures. The feasibility of the nanostructures as the sensitizer of DSSC is studied by the lowest unoccupied molecular orbital LUMO and high occupied molecular orbital HOMO of the nanostructures and the I^{-}/I_3^{-} electrolyte, and TiO2 electrode, the charge spatial separation, the energy gap. Also, the time-dependent DFT (TD-DFT) is used to investigate the optical absorptions and light-harvesting efficiency of the optimized nanostructures. The results show that all the nanostructures except azo-Al have HOMO and LUMO that satisfy the condition of sensitizers. However, only three of the eight considered nanostructures exhibit charge spatial separation. The most azo-doped nanostructures improved absorptions in the visible region. The azo doped with the sulfur atom azo-S is recognized as the most promising applicant sensitizer of DSSCs which is the most suitable LUMO and HOMO. It is characterized by charge spatial separation, low recombination rate, and good light-harvesting efficiency.

Keywords: DFT; Azo dye; Harvesting efficiency; DSSC.

1. Introduction

The burning of fossil fuels is impacting the environment adversely. Therefore, many researchers are working to find renewable and environmentally friendly energy sources. Solar energy is one of the most important renewable energy sources. The production of electricity from solar energy is the preferred method to reduce the energy crisis. The solar cell is the system designed to convert solar radiation to electricity, it is based on the photoelectric effect. The basic thing about the solar cell is the selection of the material that absorbs solar radiation. The efficiency of the materials used in solar cells to absorb solar radiation and convert it to usable electricity remains low (Zweibel, 1995). A great portion of solar radiation can be absorbed by semiconductors. When solar radiation is absorbed, electron-hole pairs are generated and then move to the cell junctions. The efficiency of silicon-based solar cells have relatively high efficiency, thus they are being presently used for the conversion of solar energy on a commercial scale. On the other hand, the high cost, the difficulty to prepare highly purified silicon, and the toxic materials used in the manufacturing process have limited their wide-reaching use. Therefore, the investigation of new sources of clean energy has become a great field of research. Dye-sensitized solar cells (DSSCs) have drawn considerable attention due to their moderately high photo-electronic efficiencies and lower manufacturing cost, thus, DSSCs have been considered one of the most favorable options to replace antiquated Si-based solar cells(O'regan and Grätzel, 1991; Cui et al., 2014; Jafari et al., 2017). The light-absorber (sensitizer such as dye), electron-transport agent (broad energy gap nano-semiconductor), and hole-transport agent (redox couple in the electrolyte) are all involved in the operation of DSSC (Zhang and Yates, 2010; Raghavan et al., 2015). Furthermore, for a DSSC to be successful, all of the system components must perform well. For a successful functioning DSSC, a sensitizer/dye should have a broad and robust absorption range from visible to near-infrared light (Ni et al., 2007; Sahoo and Roy, 2013; Nivea et al., 2014). Molecular dyes have become an important component of DSSCs, an example is the azo dyes, which are characterized by significant gains in efficiency and lifetime demonstrated over the last two decades. A large percentage of these dyes are made from natural organic resources, such as colored pigments found in fruits and other plant matter (Owolabi et al., 2020; Das et al., 2020). Many enhancements are being made to solar cells to raise their efficiency and reduced their cost (Boehe et al., 2014; Dorontić et al., 2021; Goldemberg et al., 2004). Also, DSSCs offer an expected path to reduce the price per kWh. These characteristics of DSSCs are very exciting. DSSC is based on the photosensitization created by the dyes on semiconductors such as TiO2. Published studies have shown that TiO2 and ZnO have been effectively used as photoanodes when they are used as a surface stain (Grätzel, 2004; Gao, 2008; Shi et al., 2008; Sadek et al., 2017; Taya et al., 2013). Today, azo dyes have the largest production market and are

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expected to maintain their importance in the future. Different methods are used to get the preferred color properties, yield, and particle size of the dye for enhanced dispersibility (Shankarling et al., 2017; Gürses et al., 2016; Shah, 2014; Lipskikh et al., 2018; Berradi et al., 2019). Azo dyes are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical, identical, or non-azo alkyl or aryl radicals (Gürses et al., 2016; Shah, 2014; Lipskikh et al., 2018; Berradi et al., 2019; ADIGÜZEL et al., 2017; El Harfi S and El Harfi A, 2017). Azo dyes harm humans, thus, there are efforts toward reducing or transforming them into suitable and safe products (Elshaarawy et al., 2017; Benkhaya et al., 2019). To convert solar radiation into electrical energy, a DSSC drives through three steps: It is based on photoexcitation of dyes activating an electron transfer into the conduction band of semiconductor such as TiO2, followed by regeneration of oxidized dye molecules via electron donation from the redox couple in the electrolyte, and lastly migration of electrons through the exterior load (Ganesan et al., 2008). The density functional theory DFT is used in different fields of science, and it gave results in high agreement with the experimental values (Abdulsattar et al., 2019; Abdulsattar et al., 2019; Abed et al., 2020; Al-Seady et al., 2021; Ragoussi et al., 2013). Therefore, to understand the relationship between molecular structure and its properties, DFT can be applied effectively. Theoretical calculations based on DFT can reduce time and cost. In this work, we will investigate the photosensitizer performance of azo dye and the effect of doping with (Si, Ti, S, Zn, Al, Cu, Ni) atoms in its performance. This work gives a guiding principle for the synthesis of new structures with desired properties for DSSCs. All calculations will be done theoretically by using Gaussian 09 program (Frisch et al., 2009).

2. Theory

Nanostructures from azo dye and azo doping with (Si, Ti, S, Zn, Al, Cu, Ni) atoms are constructed. These nanostructures are completely optimized using Gaussian 09 program. The quantum calculations are performed by using DFT along with the hybrid functional method (B3LYP) with the 6-31G basis set. The time-dependent density functional theory (TD-DFT) is used to examine the UV-Vis spectrum and calculate light-harvesting efficiency (LHE) by using the relation (Mehmood et al., 2015).

$$LHE = 1 - 10^{-f} \quad (1)$$

Where f oscillator strength corresponds to maximum absorption (getting from UV-Vis. spectrum). The optimized nanostructures are shown in Fig. 1.

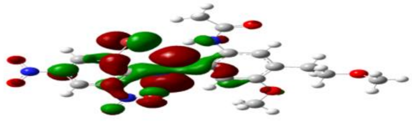
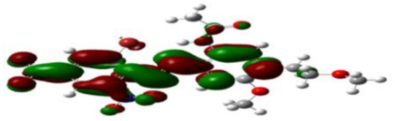
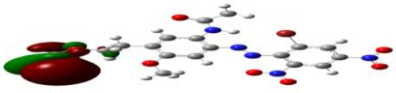
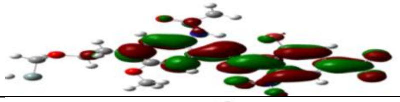
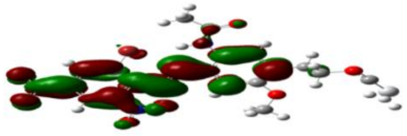
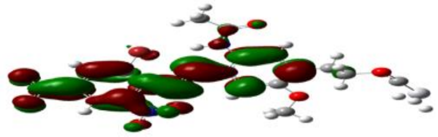
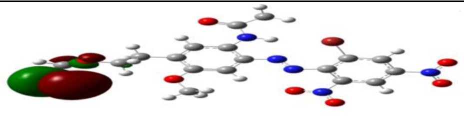
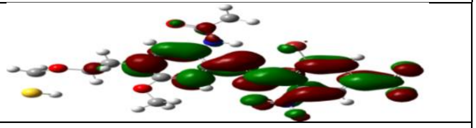
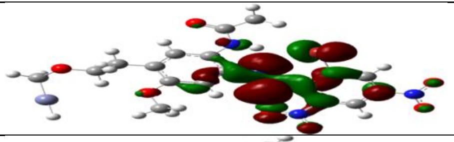
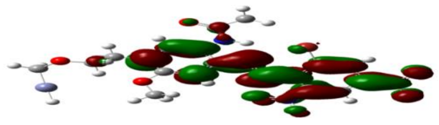
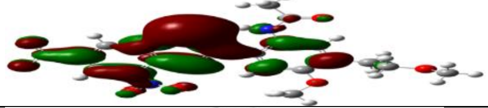
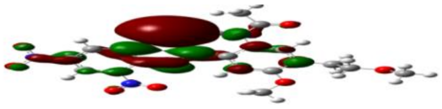
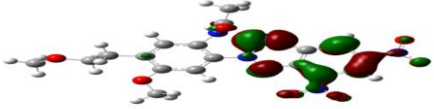
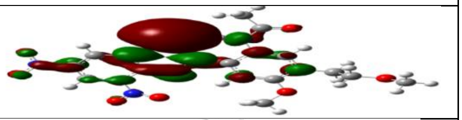
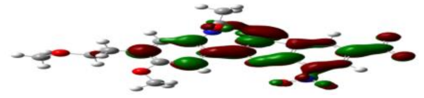
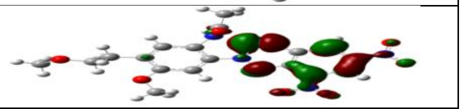
Nanostructures	**HOMO**	**LUMO**
Pure Azo		
Azo-Si		
Azo- Ti		
Azo-S		
Azo-Zn		
Azo-Al		
Azo-Cu		
Azo-Ni		

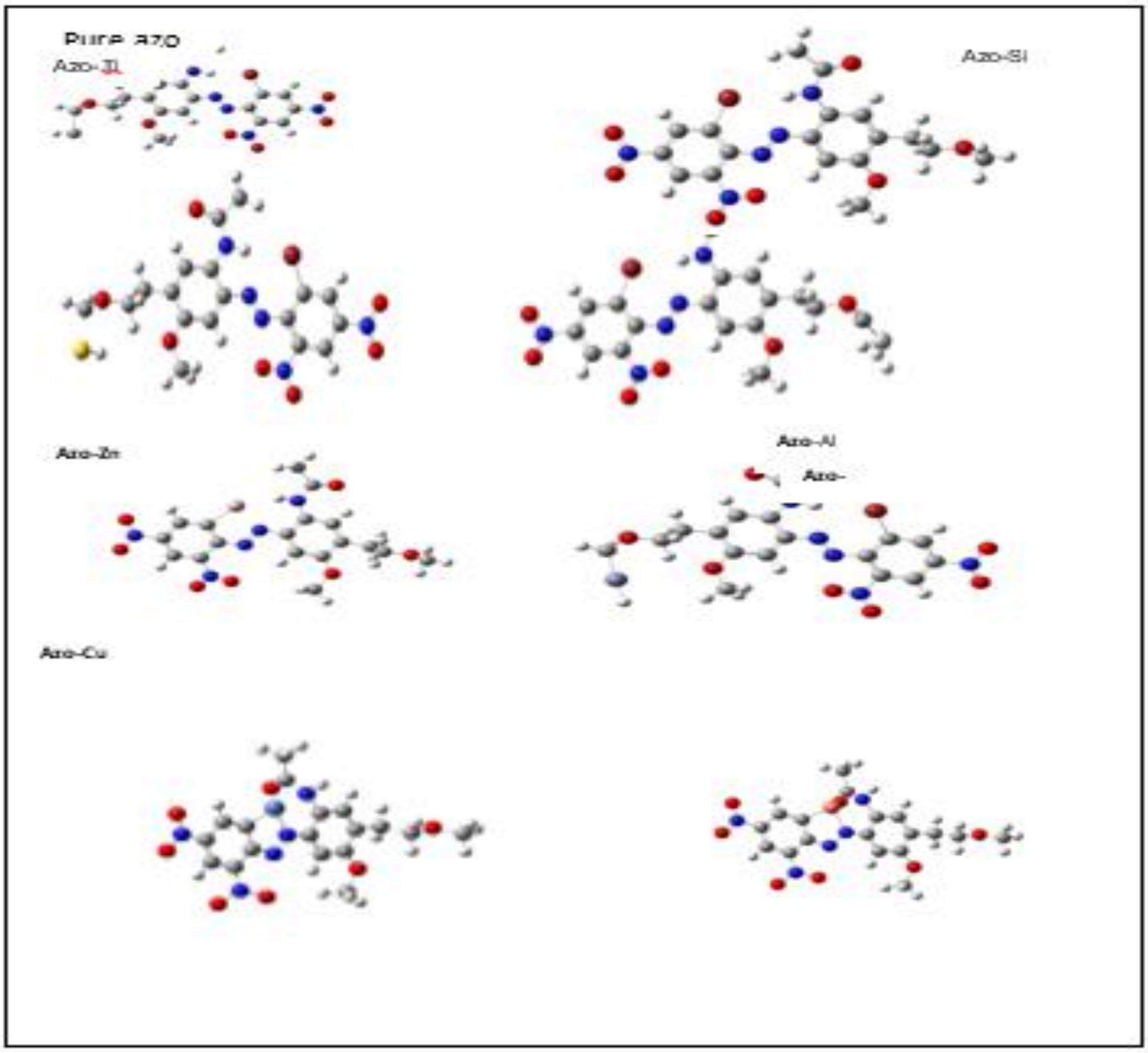
Fig. 1. The optimized azo dye doping with (Si, Ti, S, Zn, Al, Cu, Ni) atoms nanostructures

3. Results and Discussions

HOMOs, LUMOs and Energy Gaps

As the high-occupied molecular orbitals HOMOs increase there is a corresponding increase in the lower unoccupied molecular orbitals LUMOs. The HOMO-LUMO gap of the nanostructures plays a significant role in the efficiency of electron injection and the regeneration driving force (Mohammad et al., 2022). For high electron injection efficiency (high charge transfer) the HOMO level of the dye must be very near to but less than the redox potential of the $\mathrm{I}^{`}/\mathrm{I}_3^{`}$ electrolyte (−4.8 eV), while the LUMO level must be greater than the conduction band minimum CBM of TiO2 (−4.3 eV). The HOMOs and LUMOs for all the nanostructures, the CBM of TiO2 and $\mathrm{I}^{`}/\mathrm{I}_3^{`}$ redox potential levels are shown in Fig. 2. This figure illustrates that the LUMOs of all nanostructures except (azo- Al) is higher than the CBM of TiO2 and the redox energy level of $\mathrm{I}^{`}/\mathrm{I}_3^{`}$ electrolyte is greater than HOMO levels. The azo-Ti have the LUMO level (-3.887 eV) which is higher than the CBM of TiO2 (−4.3eV) and HOMO (-5.212 eV) is lower than the redox potential level of $\mathrm{I}^{`}/\mathrm{I}_3^{`}$ electrolyte (−4.8 eV), which is a confirmation that the electrons will be injected into the electrode effectively. Therefore, all the energy levels of the nanostructures except (azo-Al) satisfy the requirement of DSSCs(Gao et al. 2018; Mehmood et al., 2015).

The electron transfer from HOMO to LUMO, and the charge separation of carriers, which modify the recombination rate of the electron-hole are important two factors impacting the DSSC efficiency. Fig. 3 shows the HOMO and LUMO nanostructures and their spatial charge separation. From this figure, we note that the HOMOs of azo-Si, azo-S, and azo-Cu nanostructures are localized on the part which contains the Si, S, and Cu atoms, respectively where the Si, S, and Cu atoms are contributed as the donor. Meanwhile, the LUMOs are restricted on another side of these nanostructures. Therefore, there is apparent spatial charge separation, as a consequence, the electron-hole recombination in these nanostructures is slow, which is very favorable to the efficiency of conversion for DSSC. On the other hand, the other nanostructures clearly do not show actual spatial charge separations, on which the LUMOs and HOMOs are constrained on the similar part of the nanostructures. Thus, the spatial charge separations are minor. Hence, the recombination rate of electron-hole will be fast and the DSSCs efficiency is low. These results indicate that azo-Si, azo-S, and azo-Cu are favorable sensitizers for DSSCs.



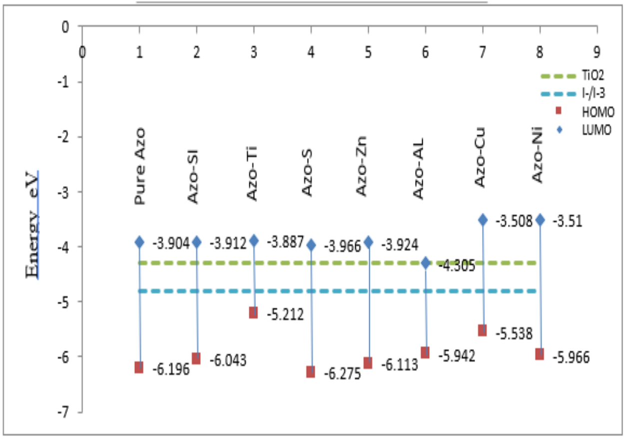


Fig. 2. Illustrations of the HOMOs and LUMOs energy levels for all the nanostructures, the CBM of TiO2, and $I^{`}/I^{`}_3$ redox potential levels.

The energy gap of the azo dye was 2.292 eV and when adding the atoms (Si, Ti, S, Zn, Al, Cu, Ni) it showed a direct effect on the values of the energy gap, as shown in Table 1, especially when adding titanium atom, the HOMO and LUMO levels of azo-Ti are higher than azo dye, therefore, the energy gap decreasing to (1.325 eV), which means that the energy bundles converge and the number of transfer electrons will be increased. The electron transfer depends on the value of the energy gap, all values of energy gaps (1.325-2.456) eV for nanostructures are suitable for electron transforms.

Table 1. Shows the HOMO, LUMO, and energy gap for nanostructures.

Nanostructures	HOMO (eV)	LUMO (eV)	Eg= LUMO- HOMO (eV)
Pure Azo	-6.197	-3.905	2.292
Azo-Si	-6.043	-3.912	2.131
Azo-Ti	-5.212	-3.887	1.325
Azo-S	-6.275	-3.966	2.309
Azo-Zn	-6.113	-3.924	2.189
Azo-Al	-5.942	-4.305	1.637
Azo-Cu	-5.538	-3.508	2.030
Azo-Ni	-5.966	-3.510	2.456

Fig. 3. HOMOs and LUMOs nanostructures.

Absorption Spectra and Light Harvesting Efficiency of Nanostructures

The absorption spectrum and light-harvesting efficiency are the important parameters for DSSCs, the absorption spectra of nanostructures are shown in Fig. 4. It is clear from the spectra that adding (Si, Ti, S, Zn, Al, Cu, Ni) atoms produced the shift of spectrum for azo dye toward the visible region for most nanostructures.

All nanostructures have good absorbance in the visible region except the azo-Ni nanostructure. The maximum wavelength (λ_{max}) corresponding to maximum intensity, oscillation strength (f), and light-harvesting efficiency (LHE) are presented in Table 2. The pure azo, azo-S, and azo-Zn nanostructures have two peaks. The pure azo, azo-Zn, and azo-Al nanostructures can be used in light-harvesting systems but are not favorable for DSSCs.

The most favorable nanostructure for DSSCs is azo-S because it has good light-harvesting efficiency, charge spatial separation, appropriate HOMO and LUMO, and suitable driving force, so that, it has satisfied all requirements for a DSSCs desired system (Gao et al. 2018).

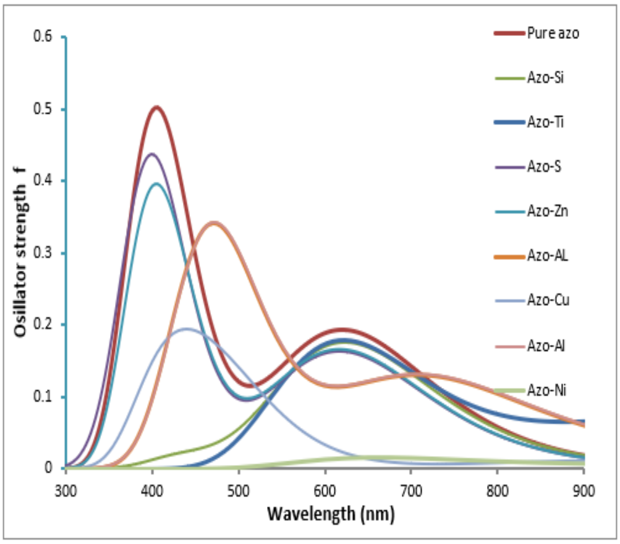


Fig. 4. UV-Vis. for nanostructures.

Table 2. λmax, f, and LHE % for nanostructures.

Nanostructures	λ_{max} nm	f	LHE %
Pure azo	406	0.502	68.522
	618.8	0.193	35.879
Azo-Si	621.6	0.176	33.319
Azo- Ti	623	0.178	33.625
Azo-S	399.2	0.437	63.44
	617.6	0.163	31.293
Azo-Zn	406	0.397	59.913
	616	0.1662	31.797
Azo-Al	472	0.342	54.501
Azo-Cu	440	0.193	35.879
Azo-Ni	650	0.0167	3.772

4. Conclusions

The geometrical optimizations and electronic properties of azo dye and the effect of doping with (Si, Ti, S, Zn, Al, Cu, Ni) atoms are investigated at the B3LYP/6-31G level. The results appear that the HOMO and LUMO energy levels of all nanostructures except (azo-Al) satisfy the requirements of DSSCs with the TiO2 electrode and $I^{`}/I^{`}_3$ electrolyte. However, only azo-Si, azo-S, and azo-Cu exhibit spatial charge separation which makes these three nanostructures favorable for sensitizer of DSSC. The results of the optical absorption spectra and light-harvesting efficiency demonstrate that the optical absorptions of azo dye are affected by doping atoms and the nanostructures. (azo-Zn, azo-S, and azo-Al) have an improvement in the visible region, indicating that they are capable to be contenders for use as harvesting materials. Moreover, azo-S nanostructure has good light-harvesting efficiency, charge spatial separation, appropriate HOMO and LUMO, and appropriate driving force. Therefore, azo-S is a favorable candidate as a sensitizer of DSSCs. These results give guidance for the design of the solar energy harvest materials and enhanced efficient sensitizer of DSSCs.

5. Declarations

Ethical Approval: Current study does not need ethical approval.

Competing Interests: The authors have no relevant financial or non-financial interests to disclose.

Authors' contributions: All authors contributed to the study conception and design. data collection and analysis were performed by [Noor Abulameer Hameed] [Hussein Hakim Abed] and [Hayder M. Abduljalil]. The first draft of the manuscript was written by [Noor Abulameer Hameed] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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