A DFT study on functionalization of acrolein on Ni-doped (ZnO)_6 nanocluster in dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells are the real substitutes to the well-established silicon-hinge solar cells owing to their greater occurrence of the photon to current transformation potency, low cost, ease of gadget invention and long-term stability [1]. The implementation of DSSC is primarily focused on the integration of photons throughout the complete visible and near-infrared regions, dye-sensitizers attached to the uppermost layer of anchoring group, the unoccupied energy level above the occupied level of PCBM and the electrolyte containing redox system [2]. The π-conjugated elements are used to stimulate the photosynthetic process on account of their superior electrochemical properties. The sensitizer interacts with the semiconductor through the PCBM, which enhances the light harvesting ability, the electron injection, the stability and the production of solar cells. Researchers are majorly concentrated on progressing dyes of structural unit donor - π - acceptor configurations [3].

The ZnO nanoparticles have attained the major attention of researchers due to their potential applications in the field of electronics, material science, and medicine [4]. The Zinc Oxide nanoparticles are highly attractive materials because it finds remarkable uses in piezoelectric devices, UV absorbers, sensors, pharmaceuticals, and cosmetic industries [5]. These nanostructured materials are of greater importance owing to their nano morphology, nontoxicity, functionality, and biocompatibility [6]. The ZnO nanostructured material has an immense band gap of 3.3 eV, which makes this material as the best semiconductor with the highest acceptance binding energy of 60 MeV in addition to low lasting threshold [7, 8]. Nano-scale Ni is a latent positive p-type semiconductor material, and its properties are one of the most important factors to influence the performance of photovoltaic devices. Doping such metal cation is an effective way to improve the electrochemical performance. This improved activity has been attributed to the enhanced separation of photogenerated electron-hole pairs due to the presence of Ni^{2+} ions in ZnO [9]. The change of semiconducting behavior of ZnO has been attributed to the Ni dopant. It has been reported that Nickel doped ZnO with a smaller crystalline size shows better electrical, optical and...
magnetic properties [10]. To further enhance the electrochemical performance of Ni-doped Zn₆O₆, Acrolein molecule is adsorbed on the surface of nano-scale NiZn₅O₆. Acrolein comprises of adjacent C=C and C=O double bonds in conjugation. The de-alder reaction of Acrolein enhances the property of interacting with NiZn₅O₆ [11, 12]. Mehdi et al. had analyzed the DFT calculations to investigate the Acrolein interaction with COOH loaded single-walled CNT [13].

A noteworthy attentiveness is on A-NiZn₅O₆ as photosensitizing dyes that are strongly absorbed the photons. The A-NiZn₅O₆ composite leads to a photoactive compound capable of electron transfer due to photoexcitation. During this investigation, the electronic structures, photovoltaic properties of A-NiZn₅O₆ were studied at various interaction sites to determine their potential effectiveness in dye-sensitized solar cells by the DFT/TD-DFT calculations. The effects of Ni doping and Acrolein adsorption on the nano-scale Zn₆O₆ have not to be reported yet. We surmise that this work will provide some basic guidelines to experimentalists to strengthen the implementation of DSSCs.

2. Theoretical methods

The geometrical framework of NiZn₅O₆ and A-NiZn₅O₆ were optimized using the B3LYP/6-31G exchange-correlation functional method with 6-31G (d,p) basis set using the Gaussian 09 program [14]. The TD-DFT computations were employed to evaluate the excitation energy, UV-Vis electronic transition, light harvesting ability and oscillator strength of photosensitizer at CAM-B3LYP/6-31G level. The HOMO/LUMO energies were analyzed at the B3LYP/6-31G level with optimized structures. The Gauss sum program was used to obtain DOS results [15]. The dipole moment, chemical parameters and polarizability were predicted from the B3LYP/6-31G functional in Gaussian 09 program. In further, molecular electrostatic potential (MEP) analysis and Mulliken charge distribution of each atom in the various sites of A-NiZn₅O₆ were also investigated by the Gaussian 09 program. The adsorption energy (Eₐd) of Acrolein on the NiZn₅O₆ at different configurations is represented by,

\[
E_{ad} = E_{A-NiZn5O6} - (E_{NiZn5O6} + E_{A})
\]

Where,

\[
E_{A-NiZn5O6} \text{ is the total electronic energy of the Acrolein adsorbed over the NiZn5O6 nanocluster,}
E_{NiZn5O6} \text{ is the total energy of the NiZn5O6 nanocluster,}
E_{A} \text{ is the total energy of the isolated Acrolein molecule [16].}
\]

3. Results and discussion

3.1. Structural properties

The complex A-NiZn₅O₆ is capable of absorbing the photons of light. Computational methods (TD-DFT/DFT) were used for characterizing A-NiZn₅O₆ with various interaction sites. The geometrical profile of NiZn₅O₆ is seen in Figure 1. The 3D structure of Zn₆O₆ was composed of two tetragonal rings faced one another that is coupled by Zn-O bonds. The Zn–O bond length identified within the pure Zn₆O₆ cluster was 2.01 Å similar to the work done by Wang et al. [17]. Replacing one of the Zinc atoms in the pure Zn₆O₆ nanocluster by Ni atom results the deformation in the bond length of Ni-O, Zn–O bonds are observed at 2.0 Å and 1.93 Å, respectively.

The Acrolein comprises of three possible interaction sites for the adsorption with NiZn₅O₆. The functionalization of Acrolein on NiZn₅O₆ cluster considered for three possible interaction sites with the functional groups of the = O Carbonyl group (C), –CH Methyl group (M₁), and –CH₂ Methylene group (M₂). The intercommunication of NiZn₅O₆ with Acrolein at three sites are seen in Figure 2.

The substitution of Ni at the 12th position of Zn in NiZn₅O₆ nanocluster for the three interaction sites exhibits the deformation in the Zn–O bond length of 1.86Å, 1.98Å, and 1.89 Å, respectively. The big difference in bond distance is observed at Zn(5)–O(7) and Zn(5)–O(4) in the C site of A-NiZn₅O₆ cluster. The bond distance of Ni–O is decreased to 1.91Å in C site. The big difference in bond distance was observed at Zn(5)–O(9), Zn(2)–O(7) and Zn(5)–O(4) in the M₁ site. The bond distance of Ni–O at the M₁ interaction site was observed as 2.0Å. The higher the difference in bond length was found at Zn (2) –O(7), Zn(5)–O(7) and O(4)–Zn(5) for the M₂ site. The bond length of the Ni–O bond was observed as 1.9Å in the M₂ site. The bond angle varies from 60° to 147° when Acrolein interacting with the NiZn₅O₆ cluster through the Ni atom. The greater bond angle difference between NiZn₅O₆ and A-NiZn₅O₆ was observed at an angle O(7)-Zn(8)-O(11), Zn(5)-O(9)-Zn(10) and Zn(10)-O(9)-Ni(12) for C site. The lower bond length of the C site of A-NiZn₅O₆ correlated with the excessive binding energy, which associated with the chemisorption mechanism [18].

The adsorption energies (Eₐd) of C, M₁ and M₂ sites of Acrolein on NiZn₅O₆ via Ni atom are calculated as -2.73 eV, -1.04 eV, -0.89 eV respectively. The Eₐd of Acrolein on the surface of NiZn₅O₆ through Zn atom and O atom are found to be less as compared to Ni atom and hence the interaction of Acrolein on NiZn₅O₆ through Ni atom is scrutinized in this manuscript. The Eₐd of Acrolein on NiZn₅O₆ via Zn atom is calculated to be -0.72 eV and via O atom is found to be -0.09 eV. The structural data consists of bond length and bond angle were listed in Table 1 and Table 2. The negative adsorption energy of the Acrolein molecule on NiZn₅O₆ is the characteristic of the chemisorption mechanism [19].

3.2. Frontier molecular orbital analysis

Figure 3 shows the spatial orientation of the frontier orbitals HOMO and LUMO, obtained by the density Functional Theory to analyze the positioning of the orbitals is revealed that the degree of HOMO density is located in the dopant atom Ni and the significant parts of the A-NiZn₅O₆ in relation to the LUMO this concentration stops at Acrolein molecule not including the methyl, methylene and carbonyl groups, these data are chemical- descriptors quantum play an important role in chemical reactions and the formation of several charge transfer complex. The orbital HOMO (Highest Occupied Molecular Orbital) measures the electron-donor character of A-NiZn₅O₆ specified by green color and the LUMO (Lowest Unoccupied Molecular Orbital) measures the electron-acceptor
character specified by red color. From these definitions, it is observed that the higher the energy of the HOMO greater electron-donating ability, and the lower the energy of the LUMO is less resistance to accept electrons. The energies of the HOMO and LUMO are used as chemical reactivity indices and are commonly correlated with other indices, such as electron affinity and ionization potential.

The HOMO and LUMO distributions of NiZn5O6 and three sites of A-NiZn5O6 computed using B3LYP/6-31G (d,p) level are shown in Figure 3. The Zn6O6 nanocluster is a broad bandgap semiconductor material. Nickel is a metal with an Eg of 0.22 eV. In the NiZn5O6 system, the HOMO and LUMO are located around the Ni atom implying that the Ni doping causes the formation of new energy levels nearer to the Fermi level. The energies of HOMO and LUMO of NiZn5O6 are -5.83 and -2.94 eV with Eg of 2.89 eV. The functionalizing compound Acrolein has a high Eg of 4.80 eV. Acrolein is introduced on the uppermost layer of NiZn5O6 and interacts via Ni atom to modify its electrical properties caused by the changes in molecular orbitals concerning their densities and energies. Upon adsorption of Acrolein, remarkable changes are observed for HOMO and LUMO distributions of A-NiZn5O6. The EHOMO and ELUMO of C, M1 and M2 sites of A-NiZn5O6 are -4.98, -3.86, -5.74, -2.99, -4.82 and -3.05 eV respectively. The Eg of the three sites are 1.12, 2.75, and 1.77 eV. In the C and M2 interaction site of A-NiZn5O6 system, the HOMO is mainly localized on the Ni center while LUMO is on the ZnO substrate which corresponds to the changes in their relative energies. The HOMO and LUMO of the M1 site of A-NiZn5O6 is situated on the acceptor end of the material. Acrolein adsorption increases the EHOMO and decreases the ELUMO of NiZn5O6. Interaction of Acrolein causes a decrement in bandgap which gives lower kinetic stability, larger electron conductivity and higher chemical reactivity make the compound to be potentially used in photovoltaic applications [20]. The photovoltaic properties were investigated for A-NiZn5O6 as a donor with PCBM as an acceptor in dye-sensitized solar cells concerning the extraordinary property of ZnO nanomaterial as a shallow donor or acceptor [20]. The EHOMO and ELUMO energies of PCBM were calculated as -6.10 eV and -3.70 eV. The LUMO magnitude of the compound A-NiZn5O6 at all the sites was more elevated than the HOMO magnitude of PCBM. The HOMO/LUMO energy, Eg, adsorption energy (Eads) and ΔEg of A-NiZn5O6 were tabulated in Table 3. By repeating all the computations by B3LYP/6-31G, B3LYP/6-311G and B3LYP/LanL2DZ level of theory, the Eg was larger than it was computed by B3LYP/6-31G.

The Acrolein decoration on NiZn5O6 causes a significant transposition of the occupied orbital to higher energy levels existed in the

Table 1. The calculated bond length of NiZn5O6, C, M1, M2 interaction site of A-NiZn5O6 at B3LYP/6-31G level of theory in the ground state analysis.

| Bond distance | NiZnSO6 | C   | M1       | M2       |
|---------------|---------|-----|----------|----------|
| Zn(1)-O(2)    | 1.934   | 1.861| 1.983    | 1.903    |
| O(5)-Zn(1)    | 1.929   | 1.861| 1.982    | 1.903    |
| Zn(1)-O(6)    | 1.931   | 1.852| 1.985    | 1.892    |
| Zn(1)-O(7)    | 1.927   | 1.853| 1.987    | 1.893    |
| Zn(9)-O(2)    | 1.922   | 1.871| 1.991    | 1.916    |
| Zn(11)-O(2)   | 1.932   | 1.864| 1.983    | 1.902    |
| O(6)-Zn(9)    | 1.939   | 1.839| 1.988    | 1.925    |
| O(2)-Ni(12)   | 2.032   | 1.912| 2.028    | 1.999    |
| Zn(3)-O(4)    | 1.927   | 1.849| 1.985    | 1.945    |
| Zn(3)-O(5)    | 1.926   | 1.864| 1.971    | 1.902    |
| O(6)-Zn(3)    | 1.939   | 1.861| 1.966    | 1.903    |
| O(4)-Ni(12)   | 2.003   | 1.913| 2.014    | 1.998    |
| O(4)-Zn(9)    | 1.929   | 1.851| 1.982    | 1.906    |
| Zn(10)-O(4)   | 1.936   | 1.866| 1.988    | 1.909    |
| Zn(11)-O(7)   | 1.935   | 1.862| 1.987    | 1.908    |
| O(8)-Zn(10)   | 1.938   | 1.868| 1.982    | 1.901    |
| O(5)-Ni(12)   | 2.007   | 1.919| 1.999    | 1.994    |
| Ni(12)-O(18)  | -       | 1.738| -        | -        |
| Ni(12)-H(16)  | -       | -    | 1.439    | -        |
| Ni(12)-H(20)  | -       | -    | -        | 1.091    |
| C(13)-C(14)   | -       | 1.54 | 1.542    | 1.544    |
| C(13)-H(16)   | -       | 1.09 | 1.092    | 1.101    |
| C(14)-H(17)   | -       | 1.096| 1.106    | 1.093    |
| C(13)-C(15)   | -       | 1.387| 1.441    | 1.432    |
| C(14)-O(18)   | -       | 1.43 | 1.432    | 1.436    |
| C(15)-H(19)   | -       | 1.092| 1.096    | 1.099    |
| C(15)-H(20)   | -       | 1.094| 1.091    | 1.101    |
middle of HOMO and LUMO of the NiZn5O6 cluster. The HOMO is extremely switched on higher energy levels, but LUMO is hardly shifted to lower energy levels. Therefore, electrons in the donor consecutively assist the higher short-circuit current density (Jsc) [22].

The highest oscillator strength of 13.8 is linked to the C site of A-NiZn5O6. The large injection potency and injection into LUMO of the acceptor. The nanocomposite A-NiZn6O6 is an efficient electron injection into LUMO of the acceptor. The theoretical value of open-circuit voltage VOC of the solar cell is calculated by,

\[
V_{OC} = |E_{HOMO} (Donor)| - |E_{LUMO} (Acceptor)| - 0.3
\]

Where, the value 0.3V is an empirical factor. The calculated Voc of C site of solar cell is calculated by,

Where Edye represents the energy of oxidation potential in the ground state at the B3LYP/6-31G(d,p) functional using the time-dependent density functional theory (TD-DFT) calculations. The \(\pi\) conjugate element A-NiZn5O6 is beneficial in decreasing the Eg and increasing the light harvesting ability. The lowest singlet to singlet excited state transition was investigated to enumerate the electronic absorption mechanisms in whole visible/near-IR regions. The A-NiZn5O6 composite showed the broad absorption of photons in the visible region and the electron excitations were observed to be \(\pi - \pi^*\) transitions. The absorption bands \(\lambda_{max}\) of NiZn5O6 and the three configurations of A-NiZn5O6 were observed at 511, 545, 448, and 459 nm respectively. The LHE can be expressed as [23]

\[
\text{LHE} = 1 - 10^{-f}
\]

Where, f is the oscillator strength of the absorption spectra of A-NiZn5O6. The highest oscillator strength of 13.8 is linked to the C site of A-NiZn5O6 in 545 nm wavelength while the modest value of oscillator strength 0.61 belongs to the M2 site of A-NiZn5O6 in 441 nm. Thus, the C site of A-NiZn5O6 shows a good light response.

3.3. Anchoring group effects on the IPCE

The short-circuit current density (Jsc) is closely connected to the charge conversion efficiency (\(\eta\)) of the solar cell is defined as,

\[
\eta = \int \text{LHE} (\lambda) \cdot \phi_{\text{inject}} \cdot G_{\text{collect}} \cdot d\lambda
\]

Where \(\text{LHE} (\lambda)\) is the light harvesting efficiency, \(\phi_{\text{inject}}\) is the electron injection potency and \(G_{\text{collect}}\) is the electron collection efficiency.

The large \(\phi_{\text{inject}}\) leads to higher short circuit current density (Jsc). The \(\phi_{\text{inject}}\) is analogous to the driving force of the electron inculcation (\(\Delta G_{\text{inject}}\)) from the photoinduced excited state of A-NiZn5O6 on the semiconductor surface and \(\phi_{\text{inject}}\) is directly proportional to the free energy of electron injected as

\[
\phi_{\text{inject}} \propto f (- \Delta G_{\text{inject}})
\]

\[
\Delta G_{\text{inject}} = E_{\text{dyne}} - E_{\text{CB}}
\]

Where \(E_{\text{dyne}}\) is the oxidative potential energy in the excited state and \(E_{\text{CB}}\) represents the reduction potential of the conduction band. \(E_{\text{dyne}}\) can be estimated by,$$E_{\text{dyne}} = E_{\text{dyne}} - \Delta E$$

Where \(E_{\text{dyne}}\) represents the energy of oxidation potential in the ground state and \(\Delta E\) is the energy of electronic vertical transition corresponding to \(\lambda_{max}\).

3.4. Spectral analysis

The correlation between the electrical conductivity and the \(E_g\) can be illustrated by,

\[
\sigma \propto \exp (E_g / k T)
\]

Where \(\sigma\) is the electrical conductivity and k is the Boltzmann constant. As the conductivity was exponentially associated with the negative rate of the bandgap, conductivity became huge as \(E_g\) was declined [24]. This equation commonly utilized to examine the sensitivity of nanostructured A-NiZn5O6. Figure 4 exhibits the DOS plots of NiZn5O6, C, M1 and M2 sites of A-NiZn5O6. The Fermi energy of NiZn5O6 is -4.38 eV. The Fermi energy of the C site of A-NiZn5O6 is calculated as -4.42 eV. The reduction in Fermi energy of the C site of A-NiZn5O6 specifies the Fermi level shifted to the valence band, which intensifies the work function. This

| Bond Angle | NiZn5O6 | C | M1 | M2 |
|------------|---------|---|----|----|
| (Zn(2)-O(1)-Zn(3)) | 92.3 | 85.9 | 95.3 | 88.1 |
| (O(1)-Zn(2)-O(4)) | 87.5 | 80.5 | 90.9 | 83.2 |
| (O(1)-Zn(2)-O(6)) | 127.1 | 119.4 | 131.2 | 121.4 |
| (O(1)-Zn(2)-O(7)) | 118.8 | 111.5 | 121.2 | 114.2 |
| (O(4)-Zn(2)-O(6)) | 62.1 | 59.34 | 65.3 | 62.9 |
| (O(6)-Zn(2)-O(7)) | 71.2 | 68.8 | 75.9 | 71.9 |
| (O(1)-Zn(3)-C(4)) | 87.3 | 81.9 | 91.3 | 84.5 |
| (Zn(2)-O(4)-Zn(3)) | 92.5 | 88.5 | 95.2 | 91.2 |
| (Zn(2)-O(4)-Zn(5)) | 135.3 | 129.6 | 138.7 | 131.2 |
| (Zn(2)-O(4)-Ni(12)) | 117.3 | 109.6 | 121.2 | 112.8 |
| (Zn(3)-O(4)-Zn(3)) | 120.8 | 112.3 | 125.2 | 115.4 |
| (Zn(3)-O(4)-Ni(12)) | 122.8 | 117.5 | 127.3 | 120.2 |
| (O(4)-Zn(5)-O(9)) | 103.9 | 97.6 | 109.5 | 106.9 |
| (O(7)-Zn(5)-O(9)) | 99 | 91.5 | 104.2 | 94.4 |
| (Zn(2)-O(6)-Zn(8)) | 104.9 | 97.5 | 110.3 | 100.1 |
| (Zn(2)-O(6)-Ni(12)) | 118.2 | 112.1 | 121.2 | 124.4 |
| (Zn(2)-O(7)-Zn(5)) | 132.3 | 128.3 | 136.7 | 139.6 |
| (Zn(2)-O(7)-Zn(8)) | 103.7 | 97.5 | 106.8 | 100.3 |
| (Zn(5)-O(7)-Zn(8)) | 79.8 | 71.1 | 84.2 | 74.3 |
| (O(6)-Zn(8)-O(7)) | 71.3 | 66.9 | 78.5 | 69.4 |
| (O(6)-Zn(8)-O(9)) | 109.7 | 101.4 | 115.4 | 104.6 |
| (O(6)-Zn(8)-O(11)) | 131.9 | 128.3 | 136.3 | 131.5 |
| (O(7)-Zn(8)-O(9)) | 100.1 | 93.2 | 106.3 | 96.2 |
| (O(7)-Zn(8)-O(11)) | 147.1 | 139.4 | 151.5 | 142.3 |
| (O(9)-Zn(8)-O(11)) | 92.78 | 84.5 | 94.5 | 87.5 |
| (Zn(5)-O(9)-Zn(8)) | 80.8 | 74.3 | 86.3 | 77.4 |
| (Zn(5)-O(9)-Zn(10)) | 140.7 | 133.8 | 146.9 | 136.8 |
| (Zn(8)-O(9)-Zn(10)) | 86.66 | 80.5 | 92.5 | 83.5 |
| (Zn(10)-O(9)-Ni(12)) | 137.6 | 130.7 | 142.8 | 133.5 |
| (O(9)-Zn(10)-O(11)) | 93.3 | 85.9 | 99.6 | 102.7 |
| (Zn(8)-O(11)-Zn(10)) | 86.6 | 79.1 | 92.3 | 95.3 |
| (O(4)-Ni(12)-O(6)) | 62.1 | 56.7 | 71.3 | 59.4 |
| (C(15)-C(14)-H(18)) | 128.7 | 132.7 | 130.2 |
| (C(14)-C(15)-O(19)) | 124.8 | 128.8 | 126.3 |
| (C(14)-C(15)-H(20)) | 89.6 | 93.6 | 91.2 |
| (C(19)-C(15)-H(20)) | 128.1 | 131.8 | 130.5 |
stimulating phenomenon makes A-NiZn$_5$O$_6$ composite detects uses in field emission properties [25].

3.6. Global reactivity descriptors

The global indices of reactivity are determined from the HOMO and LUMO energies of A-NiZn$_5$O$_6$. The $E_g$ had wider importance in understanding the static molecular reactivity and helps in characterizing the kinetic stability of A-NiZn$_5$O$_6$. The small-scale energy gap material is highly polarizable and causes the ease of transporting electrons. The reactive descriptors such as the ionization potential (IP), electron affinity (EA), electronegativity ($\chi$), hardness ($\eta$), softness ($S$), chemical potential ($\mu$), electrophilicity index ($\omega$), charge transfer ($\Delta N_{\text{max}}$), nucleofugality ($\Delta E_n$) and electrofugality ($\Delta E_e$) of NiZn$_5$O$_6$ and A-NiZn$_5$O$_6$ are computed by DFT/6-31G$^+$ and presented in Table 4.

From Koopman's theorem,

The ionization potential and electron affinity are,

$\text{I} = -E_{\text{HOMO}}$ ; $\text{A} = -E_{\text{LUMO}}$  \hspace{1cm} (9)

The prohibitive ionization energy at the M1 site indicates higher stability. The declined ionization energy at the M2 site indicates higher reactivity [26]. The reactivity of A-NiZn$_5$O$_6$ was determined through chemical hardness, chemical softness, electronegativity, and electrophilicity index. The chemical hardness of the A-NiZn$_5$O$_6$ was principally calculated as,

$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$ \hspace{1cm} (10)

The softness can be determined as follows,

$S = 1/2\eta$ \hspace{1cm} (11)

The chemical hardness and softness are the salient properties to quantify the molecular stability and reactivity [27]. The softness of A-NiZn$_5$O$_6$ at three sites is calculated at B3LYP/6-31G, 6-31G and the LANL2DZ level of theory.

The electrophilicity index values are calculated by the equation,

$\omega = \mu^2/2\eta$ \hspace{1cm} (12)

$\omega = (1+3A)^2/16(1-A)$ \hspace{1cm} (13)

Parr et.al has analyzed the electrophilicity index ($\omega$) describes the chemical reactivity of Acrolein with NiZn$_5$O$_6$ [28].

The values of HOMO and LUMO energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$), energy Gap ($E_g$) and Fermi energy ($E_F$) of NiZn$_5$O$_6$, C, M$_1$, M$_2$ interaction site of A-NiZn$_5$O$_6$ calculated at B3LYP/6-311G, 6-31G and the LANL2DZ level of theory.

| System | Method           | $E_{\text{HOMO}}$ eV | $E_F$ eV | $E_{\text{LUMO}}$ eV | $E_g$ eV | $2\Delta E_g$ eV |
|--------|------------------|---------------------|--------|---------------------|---------|-----------------|
| NiZn$_5$O$_6$ | B3LYP/6-31G     | -5.83               | -4.38  | -2.94               | 2.89    | -               |
| C      |                  | -4.98               | -4.23  | -3.86               | 1.12    | 1.77            |
| M$_1$  |                  | -5.74               | -4.36  | -2.99               | 2.75    | 1.04            |
| M$_2$  |                  | -4.82               | -3.93  | -3.05               | 1.77    | 1.12            |
| NiZn$_5$O$_6$ | B3LYP/6-311G   | -5.92               | -4.31  | -2.71               | 3.21    | -               |
| C      |                  | -4.83               | -4.26  | -3.69               | 1.14    | 2.07            |
| M$_1$  |                  | -5.8                | -4.27  | -2.74               | 3.06    | 0.15            |
| M$_2$  |                  | -4.75               | -3.78  | -2.81               | 1.94    | 1.27            |
| NiZn$_5$O$_6$ | B3LYP/LANL2DZ  | -5.9                | -4.34  | -2.79               | 3.11    | -               |
| C      |                  | -4.68               | -4.1   | -3.52               | 1.16    | 1.95            |
| M$_1$  |                  | -5.84               | -4.37  | -2.9                | 2.94    | 0.17            |
| M$_2$  |                  | -4.65               | -3.74  | -2.84               | 1.81    | 1.3             |
| PCBM   | B3LYP/6-31G     | -6.1                | -4.9   | -3.7                | 2.4     | 0.49            |

Figure 3. The HOMO/LUMO pictures of (a) NiZn$_5$O$_6$ (b) C interaction site of A-NiZn$_5$O$_6$ (c) M$_1$ interaction site of A-NiZn$_5$O$_6$ (d) M$_2$ interaction site of A-NiZn$_5$O$_6$. Table 3. The values of HOMO and LUMO energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$), energy Gap ($E_g$) and Fermi energy ($E_F$) of NiZn$_5$O$_6$, C, M$_1$, M$_2$ interaction site of A-NiZn$_5$O$_6$ calculated at B3LYP/6-311G, 6-31G and the LANL2DZ level of theory.
accepting the power of A-NiZn₅O₆ was calculated by the Eq. (9). The C
site of A-NiZn₅O₆ had the highest ω⁺ value of 15.3 eV. Thus, the C site of A-NiZn₅O₆ had the highest ability to accept electrons towards the acceptor part of A-NiZn₅O₆. The values of ω⁺ were in the order C > M₂ > M₁. The present study indicated that the lower chemical hardness, the higher electron accepting power, the better short-circuit current density of the C site consequently had a better light conversion efficieny.

The M₁ site of the nucleophile, A-NiZn₅O₆ had an electrophilicity index (ω) of 6.93 eV in opposite an electrophile C site had an electrophilicity index (ω) of 17.44 eV. The global electrophilicity index assesses the stabilization in energy when the nanocomposite A-NiZn₅O₆ gains an added charge ΔN from the surroundings [29].

\[ \Delta N_{\text{max}} = \frac{\mu}{\eta} \] (14)

The nucleofugality (ΔEn) and electrosfugality (ΔEe) are [30, 31],

\[ \Delta E_n = E_A + \omega = (\mu + \eta)/2\eta \] (15)
\[ \Delta E_e = IP + \omega = (\mu - \eta)^2/2\eta \] (16)

The chemical potential of A-NiZn₅O₆ at various basis sets are calculated by,

\[ \mu = - (E_{\text{LUMO}} + E_{\text{HOMO}})/2 \] (17)

The chemical potential of the M₂ site of A-NiZn₅O₆ was higher than the other sites with the value -3.93 eV. The electronegativity of the A-NiZn₅O₆ composite is the negative of chemical potential. The chemical potential is analogous to the electronegativity. The chemical potential and the Fermi level of A-NiZn₅O₆ are calculated at the center point of the Eg and hence the chemical potential is indistinguishable with the Fermi level of A-NiZn₅O₆.

### 3.7. Mulliken population analysis

The Mulliken atomic charges of NiZn₅O₆ and A-NiZn₅O₆ of three various interaction sites were listed in Table 5. The investigation of Mulliken charges of each atom in NiZn₅O₆ and A-NiZn₅O₆ employs DFT/B3LYP functional with a 6-31G+(d, p) basis set [32]. The Mulliken charge plot appeared in Figure 5. In the NiZn₅O₆ configuration, the atoms Zn₂, Zn₃, Zn₅, Zn₆, Zn₁₀, and Ni₁₂ possess positive charges, which are

| Property                  | NiZn₅O₆ | C  | A-NiZn₅O₆ | M₁ | A-NiZn₅O₆ | M₂ | A-NiZn₅O₆ |
|---------------------------|---------|----|-----------|----|-----------|----|-----------|
| I, -E_I eV                | 5.83    | 4.98 | 5.74      | 4.82 |          |     |           |
| A, -E_A eV                | 2.94    | 3.86 | 2.99      | 3.05 |          |     |           |
| η, -(I - A)/2eV           | 1.44    | 0.56 | 1.37      | 0.88 |          |     |           |
| μ, -(I + A)/2             | -4.38   | -4.42 | -4.36    | -3.93 |          |     |           |
| Ψ, -μ                    | 4.38    | 4.42 | 4.36      | 3.93 |          |     |           |
| S, 1/2e²V                 | 0.347   | 0.892 | 0.364     | 0.568 |          |     |           |
| ω, μ²/2e²V                | 6.66    | 17.44 | 6.93      | 8.77 |          |     |           |
| ΔNmax = μ/η               | 3.04    | 7.89 | 3.18      | 4.46 |          |     |           |
| ΔE₀ = A + ω               | 9.6     | 21.3 | 9.92      | 11.82 |          |     |           |
| ΔEe = I + ω              | 12.49   | 22.42 | 12.67    | 13.59 |          |     |           |
| Polarizability            | -113    | -131.35 | -135.9    | -139.97 |          |     |           |
| Hyperpolarizability       | 22.87   | 37.03 | 39.58     | 154.07 |          |     |           |
| Dipole Moment             | 7.16    | 6.52 | 13.16     | 7.08 |          |     |           |

Figure 4. The DOS plot of (a) NiZn₅O₆ (b) C interaction site of A-NiZn₅O₆ (c) M₁ interaction site of A-NiZn₅O₆ (d) M₂ interaction site of A-NiZn₅O₆.
Table S. Mulliken atomic charges of NiZn5O6, C, M1, M2 interaction site of A-NiZn5O6 calculated at B3LYP/6-31G level of theory.

| Atom | NiZn5O6 | CA-NiZn5O6 | M1-A-NiZn5O6 | M2-A-NiZn5O6 |
|------|---------|------------|--------------|--------------|
| O1   | -0.718  | -0.731     | -0.706       | -0.721       |
| Zn2  | 0.955   | 0.933      | 0.94         | 0.922        |
| Zn3  | 0.463   | 0.576      | 0.575        | 0.483        |
| O4   | -0.625  | -0.624     | -0.635       | -0.615       |
| Zn5  | 0.711   | 0.761      | 0.905        | 0.754        |
| O6   | -0.685  | -0.726     | -0.735       | -0.717       |
| O7   | -0.521  | -0.534     | -0.508       | -0.52        |
| Zn8  | 0.598   | 0.691      | 0.648        | 0.685        |
| O9   | -0.832  | -0.841     | -0.821       | -0.836       |
| Zn10 | 0.69    | 0.711      | 0.694        | 0.701        |
| O11  | -0.664  | -0.688     | -0.664       | -0.678       |
| Ni12 | 0.63    | 0.483      | 0.243        | 0.471        |
| C13  | -0.436  | -0.303     | -0.302       | -0.42        |
| C14  | -0.127  | -0.299     | -0.09        | -0.09        |
| C15  | 0.234   | 0.246      | 0.227        | 0.227        |
| H16  | 0.236   | 0.209      | 0.226        | 0.226        |
| H17  | 0.227   | 0.141      | 0.217        | 0.217        |
| H18  | 0.218   | 0.315      | 0.201        | 0.201        |
| O19  | -0.452  | -0.41      | -0.441       | -0.441       |
| H20  | 0.167   | 0.165      | 0.165        | 0.15         |

acceponders. The atoms O1, O2, O3, O4, O5, and O6 have positive charges, which are donors. The Oxygen O9 was more negative of -0.832e. The Zn2 atom shows a more positive charge of the value 0.955e. In the C site of A-NiZn5O6, the atoms Zn2, Zn3, Zn6, Zn12, C13, H16, H17, H18, and H20 have positive charges that are acceptors. The atoms O1, O4, O6, O7, O9, O11, C13, C14 and O19 have negative charges that are donors. The Oxygen O9 was more negative of -0.841e. The Zn2 atom has a more positive charge of 0.955e.

3.8. Molecular electrostatic potential (MEP), dipole moment and polarizability analysis

The MEP was figured out to investigate the interactions and charge distributions of NiZn5O6 and the A-NiZn5O6 complex. The MEP is a wonderful practice to envision the polarity of the individual atom present in the sensitizer compound. All isosurfaces are illustrated by the iso-value of 0.0004 e/au³ in the Gauss View program. The MEP surface prompted using the charge assignments of the nanocomposite at an atomic site is defined as,

$$V(r) = \sum \frac{z_i}{|R_i - r|} - \int \frac{\rho(r')}{|r - r'|} dr'$$ (18)

Where, ZA is the charge on the nucleus A at RA [33]. The electrostatic potential maps of NiZn5O6 and A-NiZn5O6 were presented in Figure 6. The MEP framework in Figure 6a shows that the Zn atoms and Ni atom were positively charged (blue in color) while the O atoms were negatively charged (red in color) because there was the charge shifted from Zn atoms and Ni atom to the O atoms predicting ionic bonds in the NiZn5O6 surface. Figure 6b–d show that the sector of Zn atoms was identified by the red colour, specify the negative charge because there is the charge shift from the Acrolein molecule to NiZn5O6.

The dipole moment and polarizability are useful parameters of dyes in solar cells. The dipole moment (µ) of NiZn5O6, A-NiZn5O6 at three sites and Acrolein were estimated at 7.16, 6.52, 13.16, 7.08 and 2.97 Debye. The dipole moment of C and M2 geometries were more intense than the M1 geometry. The highest deformation was observed when Acrolein decorated on the C interaction site of NiZn5O6 nanocluster. The dipole moment vector and binding energy have an inverse relationship with one another. This inverse relationship can be explained by the distance of Acrolein from the NiZn5O6 nanocluster. The larger bond length of NiZn5O6 to Acrolein predicts the lowest binding energy causes a larger dipole moment. The lower bond distance of the C site of A-NiZn5O6 predicts larger adsorption energy causes smaller dipole moment.

The polarizability (α) and the total first static hyperpolarizability (β) of NiZn5O6 and A-NiZn5O6 for all the orientations were enumerated by DFT using B3LYP/6-31G+(d,p) basis set. The first static hyperpolarizability can be narrated by the 3 × 3 × 3 matrix. The 27 constituents of the matrix declined to 10 components due to Kleinman symmetry [34].

The polarizability (α) and total first static hyperpolarizability (β) using x, y, z coordinates can be denoted by,

\[
\alpha = [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] / 3 \text{ and the average hyperpolarizability is,}
\]

\[
\beta_{\text{TOTAL}} = (\beta_{xx} + \beta_{yy} + \beta_{zz})^{1/2} \quad (19)
\]

\[
\beta_{\text{TOTAL}} = (\beta_{xx} + \beta_{yy} + \beta_{zz})^{1/2} + (\beta_{yx} + \beta_{xy})^{1/2} + (\beta_{zx} + \beta_{xz})^{1/2} + (\beta_{zy} + \beta_{yz})^{1/2} \quad (20)
\]

The mean polarizability (α) and total static hyperpolarizability (β) of NiZn5O6 and A-NiZn5O6 were collected in Table 4. The isotropic polarizability of A-NiZn5O6 was decreased as compared to the NiZn5O6 cluster. The βyy and βzz components subscribe to a huge part of hyperpolarizability in A-NiZn5O6. The βyx and βxy components donate a large part of hyperpolarizability in NiZn5O6.

Figure 5. Mulliken atomic charge plot of NiZn5O6 and C, M1, M2 interaction sites of A-NiZn5O6 calculated at B3LYP/6-31G level of theory.

![Figure 5. Mulliken atomic charge plot of NiZn5O6 and C, M1, M2 interaction sites of A-NiZn5O6 calculated at B3LYP/6-31G level of theory.](image-url)
3.9. Vibrational analysis

The IR frequencies also furnish the confirmation of the existence of powerful synergy between the Acrolein molecule and NiZn$_5$O$_6$. Assignments that involve NiZn$_5$O$_6$ cluster coordinates in the Acrolein molecule of C1 symmetry are based strictly on the DFT, B3LYP/6-311G (d,p) analysis. There are 30 possible modes of vibrations that were present in the NiZn$_6$O$_6$. The absorption peaks at 430 cm$^{-1}$ and 547 cm$^{-1}$ have corresponded to the Zn–O stretching vibrations in a simulated IR spectrum of NiZn$_5$O$_6$. The stretching vibration of Ni–O was observed in 451 cm$^{-1}$. In the theoretical spectrum of A-NiZn$_5$O$_6$, C–O stretching is found in the region of 1863 cm$^{-1}$. In previous work, the frequency of C–C stretching vibration of Acrolein has been reported as 1158 cm$^{-1}$ [35, 36]. In the geometrical parameters of A-NiZn$_5$O$_6$, the band 1007 cm$^{-1}$ assigned to C–C stretching vibration with strong intensity. The two higher wavenumbers 2987 cm$^{-1}$ and 2934 cm$^{-1}$ were assigned to the C–H stretching with strong intensity. The weak C–H stretching vibration was assigned to 3020 cm$^{-1}$ and 3054 cm$^{-1}$. In the spectral region of 1530–1420 cm$^{-1}$ infrared band was assigned to HCH vibrational modes. Furthermore, a Zn–O stretching mode of A-NiZn5O6 was shifted towards the higher wavenumber region as compared to NiZn$_5$O$_6$. The mode calculated at 1546 cm$^{-1}$ assigned to C=C stretching with strong intensity.

4. Conclusion

The computational investigation of NiZn$_5$O$_6$, C, M$_1$ and M$_2$ sites of A-NiZn$_5$O$_6$ have been studied to determine their potential efficiency in solar cells compared with the anchoring group PCBM. The molecular geometries, $E_g$, and HOMO and LUMO densities have been evaluated using DFT calculations for four new dyes. The excitation energies, absorption properties such as maximum wavelength, oscillator strength and the light harvesting efficiency of dyes have also been studied by TD-DFT calculations. The anchoring properties of the dyes and the potency of electron injection were investigated by the evaluation of polarizabilities. The C interaction site of A-NiZn$_5$O$_6$ with a small band gap built it a promising nanocomposite in photovoltaic applications than other dyes. The chemical reactivity parameters such as electrophilicity, chemical hardness, and electron accepting power proved that the C site of A-NiZn$_5$O$_6$ has high conversion efficiency. Absorption over a wide range of wavelengths due to the intramolecular π-π* interaction, extending into the near-IR region due to a small HOMO-LUMO energy gap proved that the C site is harvesting a large fraction of the solar spectrum, which in turn produces a high photocurrent and thus highly efficient solar cell performance than M$_1$ and M$_2$ dyes. Our results strongly suggest that the A-NiZn$_5$O$_6$ dyes can be successfully designed for use in DSSCs and further demonstrate the promising performance of DSSCs based on dye sensitizers. We believe that our results may provide basic guidelines for further theoretical and experimental study.

Declarations

Author contribution statement

S. Dheivamalar: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.
K. Bansura Banu: Performed the experiments; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.
Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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