Density functional theory of Ni-doped (10, 0) single-walled carbon nanotubes for C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} sensing

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Abstract. The adsorption of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} gas molecules on Ni-doped single-wall carbon nanotubes (Ni-SWCNT (10, 0)) was investigated using Density functional theory (DFT). To discover the highest interaction energy, three Ni-SWCNT configurations that are bridge, hollow, and top position of Ni on SWCNT were calculated. The Ni on the bridge configuration was the most stable configuration based on binding energy and Ni-C bond length analysis. With the addition of Ni to SWCNT, the energy gap energy of SWCNT becomes narrower from 0.879 eV to 0.289 eV. The C\textsubscript{2}H\textsubscript{4} adsorption energy was acquired stronger than C\textsubscript{2}H\textsubscript{2}, which results in a smaller energy gap. Also, the geometry change of the gases/Ni-SWCNT was investigated in this research.

Keywords: Density functional theory, C2H2, and C2H4 gas molecules, Ni-doped single-wall carbon nanotubes, binding energy, the energy gap

1. Introduction
Hydrocarbon gas is a critical gas and is widely used in everyday life applications and can be produced from natural processes or industrial output processes. Acetylene (C\textsubscript{2}H\textsubscript{2}) and ethylene (C\textsubscript{2}H\textsubscript{4}) are a type of hydrocarbon gas that is flammable, toxic, but colorless. Aside from its explosive nature, it turns out that ethylene is widely used in industry and agriculture as in the process of fruit maturity. Because of this nature, we need a tool such as sensors that can detect these gases presence so that unwanted things can be avoided.

The development of material for gas sensors is continued, particularly material with high sensitivity. The use of nanomaterials is a promising approach to achieving acetylene and ethylene gas sensors with high sensitivity and excellent gas adsorption characteristics. Some sensor materials are developed by researchers, such as piezoelectric [1], infrared [2], paper-based cataluminescence (CTL) for ethylene [3], and Au/MWCNTs [4], ZnO quantum dots [5], Pt/ZnO thick films [6], and LaFeO3 [7] for acetylene. Carbon nanotube (CNT) is a promising material as a sensor material among the sensor materials above. CNT has an essential role in nanomaterials due to its mechanical, thermal, electrical, and magnetic properties. Sometimes a metal-based catalyst is needed to improve the sensor's adsorption ability. Previous research has been carried out using Fe as a catalyst [8]. This research will use Ni as a catalyst [9] because Ni is a transition metal proven to be a suitable catalyst. Modifying the CNT with the noble metal is very effective in preparing sensitive sensors. This paper will be carried out on the SWCNT / Ni analysis to interact with C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} gas. A more detailed analysis of geometry, energy adsorption, and Density of states (DOS) is presented. This result would be useful to proposes Ni-SWCNT as an active material for hydrocarbon gas sensors.

2. Methodology
In this study, a Single-wall carbon nanotube (SWCNT (10,0)) consisting of 80 C atoms correspond to two unit cells with a diameter of 7.916Å. Ni atomic doping will be introduced to improve SWCNT’s
adsorptive capacity. Ni doping is done in two ways, doped and decorated. Doped means modifying the SWCNT structure by replacing one of the C atom of SWCNT with one Ni atom, while decorated means Ni atom is added on the surface of the SWCNT structure. Calculations are performed using the Density functional theory (DFT) method in the Vienna Ab initio simulation package (VASP) program. We use generalized gradient approximation (GGA) in the form of functional exchange-correlation Perdew-Burke-Ernzerhof (PBE) to calculate the exchange-correlation energy. The relaxation calculation is performed for the optimization structure. Monkhorst-pack points used are 1x1x6, Cut off energy 520 eV, and the level of accuracy is done up to 0.001 meV.

The calculation result will be analyzed through energy analysis, such as adsorption energy, interaction energy, and formation energy, to find the most stable structure constructed. The density of states (DOS) analysis will also be given to see the system’s electrical properties.

Adsorption energy $E_{ad}$ can be done with equation 1:

$$E_{ad} = E_{SWCNTNi+gas} - E_{SWCNTNi} - E_{gas}$$

Interaction energy $E_{int}$ for each configuration of Ni-decorated SWCNT is calculated using eq 2:

$$E_{int} = E_{SWCNTNi} - E_{SWCNT} - E_{Ni-atom}$$

Based on the literature [10], the formation energy $E_f$ can be calculated using eq 3:

$$E_f = E_{SWCNTNi} - E_{SWCNT} - E_{Ni-atom} + E_C$$

where $E_{SWCNTNi+gas}$, $E_{SWCNT Ni}$, $E_{gas}$ are the total energy from the calculation of interactions between SWCNT-Ni and gas, the total energy isolated SWCNT-Ni, and the total energy of isolated gas, respectively, while $E_{SWCNT}$ is the total energy of pristine SWCNT, $E_{Ni-atom}$ is Ni total energy/atom, and $E_C$ is total energy/atom for C in pristine SWCNT.

3. Result and discussion

3.1. Pristine SWCNT

The SWCNT used in this research is SWCNT (10,0), which has a large energy gap of 0.88 eV. An energy gap of 0.879 eV was obtained from the calculation results (figure 1). These results are close to the literature[11]. The calculation result also showed that the energy /atom for pristine SWCNT is -9.094 eV.

3.2. Ni-decorated SWCNT

Ni-decorated SWCNT structure is constructed by placing Ni on top of the SWCNT structure. Three-position of Ni is considered, such as on top of one C atom of SWCNT (top configuration).
Figure 1. DOS of SWCNT (10,0).

On the bridge of the C-C atom of SWCNT and on the hollow of SWCNT (hollow configuration) (see figure 2). These three possible positions are constructed to find the most stable positions of Ni-decorated SWCNT.

Figure 2. Three possible positions of Ni-decorated SWCNT (a) bridge, (b) hollow, (c) top.

From Table 1, it is obtained that the bridge position has the minimum interaction energy (-1.949 eV). Therefore this position will be used to calculate interactions with gases (figure 2 (a)). This position will be called Ni-decorated CNT. The DOS curve for Ni-decorated SWCNT for the bridge position can be seen in figure 3. From the curve obtained energy gap width of 0.289 eV. Energy gap results obtained are much reduced when compared to pristine SWCNT. This proves that Ni is very influential when placed close to SWCNT. Although it is still in the semiconductor category, the energy gap width is much reduced.

Table 1. Interaction energy for Ni-decorated SWCNT configurations

| Hollow  | Top    | Bridge |
|---------|--------|--------|
| -1.788 eV | -1.947 eV | -1.949 eV |
3.3. Ni-doped SWCNT

The geometry of Ni-doped SWCNT can be seen in figure 4.

From equation 3, the formation energy of Ni-doped SWCNT is -0.094 eV. DOS analysis of the doped Ni SWCNT can be seen in figure 5. The energy gap width obtained is very small at 0.194 eV, lower than the Ni-decorated SWCNT.

3.4. Interaction with gases

The two SWCNT Ni configurations then interact with C$_2$H$_2$ and C$_2$H$_4$ gas. From the results of the relaxed calculation, the position is obtained as in figure 6. The values obtained as in Table 2 are based on the energy adsorption calculation results using equation (1). From the table, it can be seen that the one that has the minimum calculation adsorption energy is C$_2$H$_4$ on Ni-decorated SWCNT. The Density of states (DOS) interactions between each gas and SWCNT-Ni also were analyzed to verify the result. DOS curves can be seen in figure 7.
Figure 5. DOS of Ni-doped SWCNT.

For each Ni-decorated SWCNT with C₂H₂ and C₂H₄, shows an energy gap width of 0.288 eV and 0.768 eV, whereas for Ni-doped SWCNT with C₂H₂ and C₂H₄, 0.288 eV and 0.192 eV are respectively. From the data, the interaction between Ni-decorated SWCNT and C₂H₄ appears to have the smallest energy gap. The results obtained are in accordance with the adsorption energy results where Ni-decorated SWCNT with C₂H₄ also has the minimum adsorption energy.

Figure 6. Relaxed position of Ni-SWCNT with C₂H₂ dan C₂H₄.
### Table 2. The adsorption energy of gases on Ni-decorated/doped SWCNT

|                | Adsorption energy (eV) | $E_{\text{Fermi}}$ (eV) |
|----------------|------------------------|--------------------------|
| Ni-decorated SWCNT with $\text{C}_2\text{H}_2$ | -1.95                  | -3.07                    |
| Ni-decorated SWCNT with $\text{C}_2\text{H}_4$ | -2.13                  | -3.43                    |
| Ni-doped SWCNT with $\text{C}_2\text{H}_2$   | -1.06                  | -3.43                    |
| Ni-doped SWCNT with $\text{C}_2\text{H}_4$   | -0.88                  | -3.20                    |

### Figure 7. Density of states of the interaction of gases with Ni-SWCNT.

#### 4. Conclusion

Using DFT calculations, the adsorption geometry, adsorption energy, and Density of states are investigated. The most optimal placement for Ni-decorated positions on SWCNT is placing it in the bridge position based on the interaction energy. Interaction of $\text{C}_2\text{H}_2$ gas with Ni-decorated SWCN has an energy gap of 0.288 eV with adsorption energy -1.95 eV. When viewed from the value of the adsorption energy, the one with the minimum value or the one with the strongest interaction with SWCNT / Ni is $\text{C}_2\text{H}_4$ gas, which is **-2.13 eV**.

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