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**Full Length Article**

**Transition metal decorated ZnO monolayer for CO and NO sensing: A DFT + U study with vdW correction**

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**Highlights**

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Pristine ZnO ML shows weak [physisorption](https://www.sciencedirect.com/topics/chemistry/physisorption) with CO/NO gas.

* •

The most stable decoration sites are the same for TM atoms (Fe, Co, Ni, Cu).

* •

Transition State Search confirms stability of adsorption and decoration sites.

* •

TM decorated ZnO ML is applicable for either sensing or capturing CO/NO atom.

**Abstract**

Based on density functional theory, we study the adsorption of CO and NO gas molecules on transition metal (Fe, Co, Ni, Cu) decorated ZnO monolayer (ZnO ML), with the electronic interactions taken into account by introducing Hubbard potential (U) for *d*-orbitals and van der Waals interactions corrected using Grimme method. From its electronic properties and adsorption energies, pristine ZnO ML shows weak physical interaction with the gas molecules with adsorption energies of −0.05 eV and −0.07 eV for CO and NO respectively. TM atoms are then placed in their most stable site (top of O atom for all TMs), with their binding energy in the range of 1.002–2.314 eV. Upon TM decoration, CO shows an adsorption energy in the range of −0.3 eV to −1.3 eV, while NO adsorption energies are in the range of −1.7 to −2 eV. Recovery time calculation shows that Fe and Co-decorated ZnO ML served as a reusable sensor for CO gas while the rest shows great application prospects in the field of industrial safety monitoring. These results showed that TM-decoration in ZnO ML is an effective way of improving its CO and NO gas sensing properties and adsorption capacities.

**Graphical abstract**



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**Introduction**

Sensing small gas molecules is a crucial step in controlling environmental pollution, and also finds application prospect in the field of medical diagnosis and industrial safety monitoring [1], [2]. An ideal sensor having high selectivity, low noise, low power consumption, high recovery time, high limit of detection, low cost and rapid response is utmost desirable for effective sensing [3], [4]. Over the years, attempts have been made to discover materials that exhibit one or more of these characteristics, such as metal oxide semi-conductors [5], [6], [7], [8] and graphene [9], [10]. Despite having promising characteristics, high power consumption and lack of selectivity restrict metal oxides from sensor applications [11]. Also, absence of band gap in pure graphene is known to restricts its applications in various aspect. However, large surface area and high sensitivity (attributed to high electron mobility at room temperature) in graphene still makes them one of the most promising candidate for sensor applications [12]. This results in the modification of graphene’s surface [13], [14], [15] and the search for other two dimensional materials having graphene like properties but with inherent bandgap and sensing ability, such as h-BN [16], [17], germanene [18], MoS2 [19], CN [20], arsenene [21], transition metal dichalcogenides (TMDCs) [22], [23], PbSnS2 [24], tellurene [25], SbP [23] and many others. These studies provide the possibility of using low dimensional graphene like material for sensing under different scope, and additionally presenting the opportunity to enhance its properties.

Among the graphene like materials, ZnO monolayer is thoroughly investigated in recent years over certain areas [26], [27], [28], [29], [30], [31], [32], [33], [34]. These studies revealed its tunable properties by means of defects, adsorption, doping, surface modification and application of strain. For instance, Lei et al*.* [31] shows that transition metal (TM) decoration is one promising way of tuning the electronic and magnetic properties of ZnO monolayer. Similarly, tuning such properties are also achieved by Chen et al. [29] using noble metal adsorption. Surface modification of two-dimensional materials by means of decoration has been known to improve its gas sensing abilities, particularly with transition metals [15], [32], [35], [36], [37], [38], [39], [40], [41]. As such, noble metal decorated ZnO monolayer is further investigated by Qu et al. [42] for its performance over gas sensing, which proves to be effective for the adsorption of CO, NO and NH3. These studies motivate decoration of ZnO monolayer to further improve its adsorption and gas sensing properties, particularly for diatomic molecule such as CO and NO which are highly toxic, colorless and odorless in the atmosphere. Apart from its hazardous effect on the environment, high concentration of these diatomic molecules can have adverse effect on human health [43], [44]. Following the works that had been done for CO and NO sensing over the years [15], [34], [37], [38], [39], [40], [42], [45], transition metal decorated ZnO is investigated in this study. With single unpaired electrons in CO and NO, which makes them chemically reactive, we hope to provide additional stabilities with the embedded TM atoms.

Based on density functional theory, we have studied the adsorption properties of TM decorated ZnO ML, with its electronic interactions taken into account by introducing Hubbard potential (U) for *d*-orbitals. Most stable configuration of CO and NO adsorbed-pristine ZnO ML is first investigated. Electronic, magnetic, adsorption energy and its recovery time are then calculated for comparison with the decorated system. TM (Fe, Co, Ni, Cu) atoms are introduced on top of ZnO monolayer, which shows the same optimal decoration site for all the TM atoms. CO and NO gas molecules are then placed on top of the decoration and its electronic properties are investigated to reveal the interactions between the systems. Our study shows that TM-decorated ZnO ML shows significant improvement in adsorption of the diatomic molecules with extreme sensitivities and large adsorption energies in comparison with its pristine adsorption. The results as presented in this work show that Co decorated ZnO ML is most suitable for CO gas sensor owing to its short recovery time of 16.98 s, which enables easy recycling of the sensor.

**Section snippets**

**Computational details**

All the calculations are performed within the framework of spin-polarized plane-wave density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [46] within General Gradient approximation (GGA) as revised by Perdew, Burke and Ernzerhof [47]. Projector Augmented Wave (PAW) [48] was used to handle interactions between ions and electrons. Spin polarization and dipole moment corrections are also considered in this study.

The orbital-dependent on-site Coulomb

**Pristine ZnO monolayer**

A 3 × 3 supercell ZnO monolayer is cleavage from a bulk wurtzite ZnO structure with (0001) polar surface and then structural optimization is performed. Optimized ZnO monolayer, shown in Fig. 1(a) possess a planar graphene like structure with bond length of 1.905 Å, comparable to previously reported theoretical values of 1.8–1.9 Å [26], [27], [30], [58] and experimental values of 1.92 Å [59]. Charge density distribution depicted in Fig. 1(b) shows that charges are denser around Zn atom

**Conclusion**

In summary, pristine ZnO ML shows weak physical interaction with the gas molecules even at its optimal adsorption site, i.e., center of hexagon for CO and top of Zn atom for NO, with adsorption energies of −0.05 eV and −0.07 eV for CO and NO respectively. However, decoration of transition metal (Fe, Co, Ni, Cu) atom greatly enhanced the adsorption capacity of ZnO ML. Upon TM decoration, CO shows adsorption energies in the range of −0.3 eV to −1.3 eV, while NO adsorption energies are in the

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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