First-Principles Insight into Pd-Doped ZnO Monolayers as a Promising Scavenger for Dissolved Gas Analysis in Transformer Oil

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ABSTRACT: ZnO monolayers with desirable n-type semiconducting properties are full of potential for sensing applications. In this work, we investigate using first-principles theory the adsorption and sensing behaviors of Pd-doped ZnO (Pd-ZnO) monolayers with two typical dissolved gases, namely, H₂ and C₂H₂, to explore their sensing use for dissolved gas analysis in transformer oil. For Pd doping on the pristine ZnO monolayer, the T₀ site is identified as the most stable configuration with an E_b of −1.44 eV. For the adsorption of H₂ and C₂H₂, chemisorption is determined given the large adsorption energy (E_ad) and formation of new bonds. Analyses of the charge density difference and density of state provide evidence of the strong binding force of Pd−H and Pd−C bonds, while band structure analysis provides the sensing mechanism of the Pd-ZnO monolayer as a resistance-type sensor for H₂ and C₂H₂ detection with high electrical responses. Also, analysis of the work function (WF) provides the possibility of selective detection of H₂ and C₂H₂ using a Pd-ZnO monolayer-based field-effect transistor sensor given the opposite changing trend of the WF after their adsorption. Our work may broaden the application of ZnO-based gas sensors for application in the field of electrical engineering.

1. INTRODUCTION

Due to the zero band gap property of graphene, which prevents its applications in nanoelectronics and optics,¹,² scholars have attempted to explore novel two-dimensional (2D) nanomaterials with an in-plane hexagonal structure and outstanding electronic behavior.³,⁴ In recent years, zinc oxide (ZnO), one of the II-VI compounds, has attracted great attention because of its desirable n-type semiconducting property.⁵ Increasingly, graphene-like ZnO is explored and theoretically investigated with unique electronic and optical properties,⁶–⁸ indicating its superior potential for gas sensing, energy storage, and catalysis. Moreover, it has been reported that single-layer and bilayer ZnO could be experimentally prepared by the deposition of Zn on a Au (111) surface using X-ray photoelectron spectroscopy and scanning tunneling microscopy,⁹ which stimulates the study of ZnO monolayers as a novel 2D member for application in many fields.

For voltage transformers in the transmission line,¹⁰ electrical transformers are the most significant and expensive equipment in the power system. Currently, oil-immersed transformers account for over 90% of transformers in the engineering field, and oil is the insulation media to guarantee their safe operation.¹¹ In a long-running transformer, however, inevitable insulation defects will cause partial overheating and partial discharge to the inner part of the devices,¹² decomposing the oil into several gas species, including H₂, CH₄, C₂H₂, and C₂H₄ dissolved in the oil.¹³–¹⁵ As a result, the insulation performance of the oil would deteriorate causing serious power accidents such as oil spills, massive blackout, and even explosion of the transformers.¹⁶,¹⁷ Therefore, dissolved gas analysis (DGA)¹⁸ is proposed through sensing the dissolved gases in the transformer oil to evaluate the operation status of such devices.¹⁹ Undoubtedly, the gas sensing method with

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advantages of a rapid response, high sensitivity, and low cost is considered to detect these characteristic gases and has been deemed as one of the most workable approaches for the DGA end.\(^{20,21}\)

To the best of our knowledge, there has been few reports regarding the exploration of a ZnO-based gas sensor for DGA, and the large surface area of the 2D ZnO monolayer upon gas interaction allows its application as gas sensors.\(^{22,23}\) As reported, a transition metal (TM)-doped ZnO monolayer performs enhanced sensing and catalytic performance in gas interactions,\(^{24,25}\) as the TM dopants usually promote the electron mobility and charge transfer of the nanosystem. This would be beneficial to increasing the sensing response of a TM-ZnO monolayer as a gas sensor. Given the desirable catalytic behavior of a Pd dopant,\(^{26,27}\) this work proposed a Pd-doped ZnO (Pd-ZnO) monolayer as a gas sensor for the detection of two typical dissolved gases (H\(_2\) and C\(_2\)H\(_2\)) with a predominant content in transformer oil.\(^{28}\) We first studied the Pd-doping behavior on the pristine ZnO surface and simulated the adsorption performance of a Pd–ZnO monolayer with the H\(_2\) and C\(_2\)H\(_2\) molecules. Subsequently, the sensing mechanism of our proposed material is analyzed to illustrate its potential for application in the field of electrical engineering. This work may broaden the pathway for a TM-doped ZnO nanostructure for preparing electronic devices such as chemical sensors.

### 2. COMPUTATIONAL DETAILS

All the calculations in this work were implemented in the Dmol\(^3\) package,\(^{29}\) which adopted the Semi-core Pseudopotential treatment with the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange correlation functional.\(^{30}\) The DFT-D2 (Grimme) method was applied to understand the van der Waals force and long-range interactions.\(^{31}\) Double numerical plus polarization (DNP) were used as the atomic orbital basis set.\(^{32}\) Brillouin zone sampling was set using a Monkhorst–Pack grid with a k-point mesh of \(10 \times 10 \times 1\) for both geometric optimizations and electronic calculations.\(^{33}\) The energy tolerance accuracy, maximum force, and displacement were determined to be \(10^{-5}\) Ha, \(2 \times 10^{-3}\) Ha/Å, and \(5 \times 10^{-3}\) Å,\(^{34}\) respectively. For the static electronic structure calculations, the self-consistent loop energy of \(10^{-6}\) Ha, global orbital cutoff radius of 5.0 Å, and smearing of 0.005 Ha were defined to ensure the high accuracy of the total energy.\(^{35}\)

A \(4 \times 4 \times 1\) supercell of the ZnO monolayer was established to fulfill the calculation in this work, which contains 16 Zn and 16 O atoms in total. The vacuum region was set to 15 Å to prevent the interaction between adjacent units.\(^{36}\) In addition, the Hirshfeld analysis was used to analyze the atomic charge of the Pd dopant (\(Q_{\text{Zn}}\)) in the doping process and molecular charge of charge transfer (\(Q_T\)) in the adsorption processes.\(^{37}\)

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of the Pd-ZnO Monolayer

After complete optimization, the constant lattice of the ZnO surface is obtained to be 3.30 Å with a Zn–O bond length of 1.91 Å, in agreement with the theoretical work.\(^{38}\) Figure 1 plots the Pd-doping process on the pristine ZnO surface in which four possible sites are considered, traced as T\(_{\text{O}}\) (at the top of the O atom), T\(_{\text{H}}\) (at the top of the Zn–O hexatomic ring), T\(_{\text{Zn}}\) (at the top of the Zn atom), and B\(_{\text{Zn}=\text{O}}\) (at the top of the Zn–O bond), as shown in Figure 1a. The binding energy (\(E_b\)) is defined to evaluate the force between the Pd dopant and the ZnO surface, calculated as

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c02592)
where \( E_{\text{Pd} - \text{ZnO}}, E_{\text{Pd}} \), and \( E_{\text{ZnO}} \) signify the energies of the Pd−ZnO surface, isolated Pd atom, and pure ZnO surface, respectively.

Based on our calculations, the most stable configuration (MSC) for Pd doping on the ZnO surface is through the TO site with an \( E_b \) of \(-1.44 \) eV as shown in Figure 1b, larger than that \((-1.12 \) eV\(^3\)) of Pd doping on the pristine h-BN surface, indicating the stronger binding force between the Pd dopant and O atom. After doping, the Pd dopant is captured by the O atom and neighboring Zn atoms, forming a tripod-like structure on the ZnO plane. The Pd−O and Pd−Zn bonds are measured to be 2.15 and 2.70 Å, respectively. According to Hirshfeld analysis, the Pd dopant is positively charged by 0.136e, indicating its electron-releasing behavior as proven elsewhere.\(^3\) From the charge density difference (CDD) in Figure 1c, there is dense electron accumulation on the Pd−O and Pd−Zn bonds, suggesting strong electron hybridization between Pd and O & Zn atoms that leads to the formation of new chemical bonds. From these findings, one can infer that Pd doping on the ZnO monolayer is quite stable and causes obvious electronic redistribution for this system.

Figure 2 depicts the band structure (BS) and density of state (DOS) of pristine and Pd-doped ZnO systems to illustrate the modulated electronic behavior of the ZnO surface induced by Pd doping. It is found that the band gap of the pristine ZnO surface is obtained to be 1.867 eV here, consistent with the 1.76 eV reported in ref 40 based on the PBE function. After Pd doping, there exists a novel state within the band gap of the ZnO system, therefore resulting in a narrowed band gap of 1.414 eV for the Pd−ZnO system. It is worth noting that the top of the valence band and the bottom of the conduction band of the Pd−ZnO monolayer are located on the K and \( \Gamma \) point, respectively, which evidences its indirect semiconducting property.\(^8\) This is different from that in the pristine ZnO system wherein the top of the valence band and the bottom of the conduction band are both located at the \( \Gamma \) point. In other words, Pd doping tunes the direct semiconducting property of the pristine ZnO monolayer, which might affect its optical behavior to some extent.

From the total DOS, one can see that the Pd dopant contributes largely to the states around the Fermi level, which not only creates a novel peak at the top of the valence band but also sharpens the peaks at the bottom of the conduction band. These results indicate that the electrical conductivity of the ZnO monolayer would be reduced after Pd doping on its surface. From the atomic DOS, the Pd 4d orbital is hybridized with O 2p and Zn 3d orbitals at \(-3.42, -0.38, \) and \(-1.46 \) eV, implying the electron hybridization during the formation of Pd−O and Pd−Zn bonds and their ionic bond nature. All these findings manifest the significant modulation of electronic behavior in the ZnO monolayer with stable Pd doping.

### 3.2. Adsorption of H\(_2\) and C\(_2\)H\(_2\).

Based on the MSC of the Pd−ZnO monolayer, H\(_2\) and C\(_2\)H\(_2\) adsorptions are conducted. The two gas molecules are approaching the Pd center to highlight the interactions between them. In addition, the adsorption energy \( (E_{\text{ad}}) \) is defined to evaluate the binding strength between the Pd−ZnO monolayer and the gas molecules calculated as

\[
E_{\text{ad}} = E_{\text{Pd−ZnO/gas}} - E_{\text{Pd−ZnO}} - E_{\text{gas}}
\]

where \( E_{\text{Pd−ZnO/gas}} \), \( E_{\text{Pd−ZnO}} \), and \( E_{\text{gas}} \) signify the energies of the gas adsorbed system, pure Pd−ZnO monolayer, and isolated gas molecule, respectively. We only plot and analyze the MSC for gas adsorption in the following sections. For better understanding the charge transfer and bonding...
mechanism in gas adsorption, CDD is also plotted for every adsorption configuration. For the Pd−ZnO/H₂ system as shown in Figure 3, it is seen that the H₂ molecule is adsorbed on the top of the Pd dopant with two H atoms captured and the H−H bond broken. The H₂ molecule is parallel to the ZnO plane with an equal Pd−H bond length of 1.69 Å, and the H−H bond of the adsorbed H₂ molecule is elongated to 0.86 Å from 0.76 Å in the isolated phase. These findings suggest the strong binding force between the Pd dopant and H atoms that leads to obvious geometric activation for the H₂ molecule.

Interestingly, when the H₂ molecule is put vertically on the ZnO surface on the top right corner of the Pd atom, it somewhat experiences displacements and returns to the molecule-parallel position. The E_{ads} for H₂ adsorption on the Pd−ZnO surface is calculated to be −1.08 eV, implying the desirable chemisorption here. Based on the Hirshfeld analysis, the H₂ molecule after adsorption is negatively charged by 0.047e, presenting an electron-accepting behavior when interacting with the Pd−ZnO monolayer. From the CDD, electron accumulation is highly localized on the Pd−H bonds, indicating the formation of Pd−H bonds, while electron depletion is on the Pd−O and Pd−Zn bonds, indicating their weakness after H₂ adsorption.

As shown by the Pd−ZnO/C₂H₂ system in Figure 4, one can see that the C₂H₂ molecule tends to be adsorbed on the Pd−ZnO surface at a molecule-paralal position. Two C atoms in the adsorbed C₂H₂ molecule are trapped by the Pd dopant, forming an equal bond length of 2.08 Å, and the two H atoms are slightly up-warped, making the linear molecule be bent after adsorption. In addition, the C≡C bond and C−H bonds undergo different levels of elongations in the adsorbed C₂H₂ molecule, indicating its activation in the structure during adsorption. The E_{ads} in this system is obtained to be −1.80 eV, which is much larger than that in the H₂ system, implying the stronger binding force of the Pd−ZnO monolayer with the C₂H₂ molecule. Thus, chemisorption could also be identified in the C₂H₂ system. According to the Hirshfeld analysis, the Qₜ here (−0.092e) is also larger than that in the H₂ system, illustrating the stronger electron-accepting behavior of the C₂H₂ molecule. In CDD, strong electron hybridization could be found at the Pd−C bonds where electron localization occurs. Also, the electron depletion on the C≡C bond and C−H bonds reveals their weakness in the adsorbed C₂H₂ molecule.

In short, it could be inferred that the Pd−ZnO monolayer displays stronger adsorption performance with C₂H₂ than with H₂, which we assume may be attributed to the stronger binding force of Pd−C than of Pd−H. Despite this, chemisorption could be identified for both systems given their desirable E_{ads}. After gas adsorption, the electron distribution in the Pd−ZnO system suffers a significant change, which therefore will alter its electronic behavior largely. These parts of the analyses will be given in the following section.

3.3. Electronic Behavior. Figure 5 portrays the BS and DOS of the gas adsorption systems. In the H₂ system, the band gap is widened to 1.692 eV from 1.414 eV for the pure Pd−ZnO system. This manifests the reduced electrical conductivity and the increased electrical resistance of the Pd−ZnO monolayer with H₂ adsorbed. In the total DOS, the states around the Fermi level become smoother in the H₂ system, and the bottom of the conduction band is apparently right-shifted, verifying the increased band gap from the qualitative aspect. On the other hand, the states in the valence band are not affected with remarkable deformation. Thus, we deem that the carrier concentration in the Pd−ZnO/H₂ system is reduced accordingly. From the atomic DOS, the Pd 4d orbital is hybridized with the H 1s orbital at −7.61 and 3.81 eV, confirming the formation of Pd−H bonds. However, the hybridization seems somewhat weak, which we presume is due to the weak state intensity of the H atom.
In the C\textsubscript{2}H\textsubscript{2} system, the band gap is widened to 1.522 eV, similar to that in the H\textsubscript{2} system. Thus, it can be concluded that the electrical conductivity of the Pd–ZnO monolayer would decrease after interaction with both H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2}. From the total DOS, the states of the Pd–ZnO monolayer after C\textsubscript{2}H\textsubscript{2} adsorption experience significant deformations in comparison with those of the pure counterpart, which indicates that the carriers are activated largely due to the desirable charge transfer in this system. However, the location of the bottom of the conduction band and the top of the valence band are not seen to be remarkably changed. This finding is consistent with that of the band structure that the band gap of the Pd–ZnO/C\textsubscript{2}H\textsubscript{2} system is widened only by 0.108 eV compared with that of the pure Pd–ZnO system, much lower than the wideness of 0.278 eV from the pure Pd–ZnO system to the Pd–ZnO/H\textsubscript{2} system. Therefore, one can deduce that the decrease in the electrical conductivity of the Pd–ZnO monolayer after adsorption of H\textsubscript{2} would be higher than that after the adsorption of C\textsubscript{2}H\textsubscript{2}. From the atomic DOS, the Pd 4d orbital in its electrical conductivity according to eq 3.\textsuperscript{44} Furthermore, the change in the electrical conductivity would give the possibility of application as a resistance-type sensor for gas detection. For this purpose, the sensitivity response will be analyzed in the next section to expound the exploration of Pd–ZnO monolayer as a resistance-type sensor for gas detection.

### 3.4. Resistance-Type Sensor Exploration

As is well-known, the band gap is related to the electrical conductivity of a certain material.\textsuperscript{45} In this work, the band gap of the Pd–ZnO monolayer experiences different levels of increases after adsorption of H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2}, which can lead to the decreases in its electrical conductivity according to eq 3.\textsuperscript{44} Furthermore, the change in the electrical conductivity would give the possibility of application as a resistance-type sensor for gas detection. From this regard, we presume that the Pd–ZnO monolayer could be explored as a sensor for H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} detection with sensitive responses given the desirable increases in its band gaps. To verify this hypothesis, the sensitivity (S) of the Pd–ZnO monolayer upon H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} detection is calculated based on eq 4.

\[
\sigma = A\cdot e\left(-\frac{\Delta E}{3kT}\right)
\]

\[
S = \frac{1}{\sigma_{\text{gas}}} - \frac{1}{\sigma_{\text{pure}}} = \frac{\sigma_{\text{pure}} - \sigma_{\text{gas}}}{\sigma_{\text{gas}}}
\]

In eq 3, \(\sigma\) is the electrical conductivity, \(A\) is a constant, \(k\) is the Boltzmann constant, and \(T\) is the working temperature; in eq 4, \(\sigma_{\text{gas}}\) and \(\sigma_{\text{pure}}\) represent the electrical conductivity of the Pd–ZnO/H\textsubscript{2} (Pd–ZnO/C\textsubscript{2}H\textsubscript{2}) system and pure Pd–ZnO monolayer, respectively.

Using such two equations, the \(S\) values for H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} detection by the Pd–ZnO monolayer are calculated to be up to 223.3 and 7.2, respectively. That is, the changed electrical conductivity of the Pd–ZnO monolayer would be large enough for detection by the electrochemical devices. Thus, it is believable that the Pd–ZnO monolayer could be a promising candidate for sensing H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} with admirable electrical responses.

### 3.5. Work Function (WF) Analysis

The WF describes the minimum energy required for a material to immediately dislodge an electron from its surface to the vacuum. Therefore, the WF indeed illustrates the difficulty for certain materials to release electrons; meanwhile, in a gas interaction, the WF exhibits the contact barrier of the band alignment between the gas molecule and the specific surface.\textsuperscript{46} In this section, we perform the WF analysis to evaluate the possibility of the Pd–ZnO monolayer for application as a field-effect transistor sensor.\textsuperscript{46}

Figure 6 plots the WF of the pristine and Pd-doped ZnO monolayer and those of H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} systems. From this figure, it is seen that the WF of the pristine ZnO monolayer is 5.44 eV and that of the Pd–ZnO monolayer is reduced largely to 5.12 eV. In other words, Pd doping enhances the carrier density and carrier mobility of the ZnO system, thus reducing the electron affinity of the pristine ZnO surface and making it easier to dislodge an electron from the Pd-doped surface. After adsorption of H\textsubscript{2}, the WF of the Pd–ZnO monolayer increases to 5.22 eV, while after adsorption of C\textsubscript{2}H\textsubscript{2} the WF of the Pd–ZnO monolayer decreases to 5.03 eV. These findings suggest that the electron overflow from the Pd–ZnO monolayer to the vacuum level will be impeded after adsorption of the H\textsubscript{2} molecule and will be boosted after adsorption of the C\textsubscript{2}H\textsubscript{2} molecule. Apart from that, the changed WF of the Pd–ZnO surface induced by H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} adsorption provides the possibility for gas detection by Kelvin probe microscopy that works for WF detection,\textsuperscript{46} or the field-effect transistor sensor that works by modulating the gate voltage.\textsuperscript{47} Furthermore, given the opposite changing tendency of the WF in Pd–ZnO/H\textsubscript{2} and Pd–ZnO/C\textsubscript{2}H\textsubscript{2} systems, selectivity sensing between H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} molecules. Apart from that, the changed WF of the Pd–ZnO monolayer as a resistance-type sensor for gas detection.
4. CONCLUSIONS

In this work, first-principles theory is employed to investigate the adsorption and sensing behavior of the Pd−ZnO monolayer with H₂ and C₂H₂ molecules to explore its sensing application for DGA in transformer oil. The work mainly includes three parts: (i) Pd-doping behavior on the pristine ZnO monolayer, (ii) adsorption performance of the Pd−ZnO monolayer with H₂ and C₂H₂ molecules, and (iii) sensing exploration. Our results indicate that a Pd dopant can stably be trapped on the TO site of the pristine ZnO surface with an energy of ~1.44 eV with formation of Pd−O and Pd−Zn bonds, indicating its good geometric stability. The E_a for H₂ and C₂H₂ adsorptions are obtained to be ~1.08 and ~1.80 eV, respectively, which is identified as chemisorption as supported by the CDD and DOS. The BS and WF analyses provide the sensing mechanism of a Pd−ZnO monolayer with H₂ and C₂H₂ using a resistance-type sensor with admirable electrical responses and a field-effect transistor sensor with good selectivity, respectively. Our work would be beneficial to exploring a Pd−ZnO monolayer as a novel gas sensor to be applied in the field of electrical engineering and many other sensing fields.

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Notes
The authors declare no competing financial interest.

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