การดูดซับของแอมโมเนียบนแผ่นซิงก์ออกไซด์นาโนเพื่อเป็นวัสดุรับรู้แก๊ส

Adsorption of NH_3 on ZnO Nanosheets for Gas Sensor

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Abstract

Adsorption configurations of NH_3 on single–, double–, triple– and quadruple–layer CNL–ZnOGLNS's and their adsorption energies were obtained using B3LYP/LanL2DZ calculation. Adsorption energies of CNL–ZnOGLNS' and its multi–layers species are within –28.25 to –21.52 kcal/mol. Due to NH_3 is chemisorbed on single– CNL–ZnOGLNS', the sigle– CNL–ZnOGLNS' may be applied as NH3 sensor. Energy gaps, chemical indices of CNL–ZnOGLNS' and its multi–layers species are reported.

Keywords: *adsorption energies; Gas sensor; ZnO–nanosheet; ammonia*

บทคัดย่อ

ศึกษาการดูดซับของแก๊สแอมโมเนียบน แผ่นนาโนชีทของซิงก์ออกไซด์ชนิดคล้ายโคโรนีน หนึ่งชั้น, สองชั้น, สามชั้น และสี่ชั้น โดยการคำนวณด้วย B3LYP/LanL2DZ รายงานค่าพลังงานการดูดซับของแผ่นนาโนของซิงก์ออกไซด์ชนิดคล้ายโคโรนีนและชั้นต่างๆ มีค่าอยู่ระหว่าง –28.25 ถึง –21.52 กิโลแคลอรีต่อโมล พบว่าNH3 บนแผ่นนาโนซิงก์ออกไซด์ชนิดคล้ายโคโรนีหนึ่งชั้นเท่านั้นที่ถูกดูดซับทางเคมี ทำให้สามารถนำไปเป็นวัสดุรับรู้แก๊สแอมโมเนียได้ และได้ศึกษาค่าแถบพลังงาน และค่าดัชนีเคมีกัล

คำสำคัญ: *พลังงานการดูดซับ; วัสดุรับรู้แก๊ส; แผ่นนาโนซิงก์ออกไซด์; แอมโมเนีย*

Introduction

ZnO is an n–type semiconductor material with energy band gap of 3.3 eV and oxygen–adhesive energy of 60 meV at temperature [1, 2], can be used as UV sensor [3–6], electronic device, solar cell and short–wavelength photoelectronic. Due to its electrical conductivity and light transparency, ZnO is used as light diode, laser diode, photocatalyst and UV–filter.

NH_3 is a compound of nitrogen and hydrogen. NH_3 is a high toxicity to human. The determination of NH_3 is process controlling in industrial, agricultural and medical fields. NH_3 gas sensors have been improved to use semi–conducting metal oxides and concucting polymer [7, 8].

In this work, we aim to study and find an appropriated structure of CNL–ZnO' graphene–like nanosheets for gas sensor using quantum chemistry calculation.

Theory

Density function theory is a method based on calculating a ground state electron using LanL2DZ as a basis set. This calculation is an effective core potential (ECP) type considering electron in two parts, which are inner electron and valence electron.

Literature reviews

There were many researches reported about study of ZnO

In the 2004, Wang et al. [7] studied multi–walled carbon nanotube for detecting gaseous molecules of NH_3 using microwave phasma–enhanced chemical vapor deposition. They found that the gas sensor is highly sensitive to NH_3 molecule at room temperature.

In the 2008, An et al. [9] studied adsorption of oxygen, nitrogen, carbonmonoxide, ammonia and nitrogendioxide on ZnO nanotube using density functional theory. They found that interaction of O_2 and H_2 molecules are physisorbed while CO, NH_3 and NO_2 were chemisorbed.

In the 2012, Kaewruksa et al. [10] studied adsorption of H_2O and NH_3 on ZnO hydrogen–terminated ZnO nanoclusters and ZnO graphenelike–nanosheets using density functional theory. They found that adsorption energies of ZnO nanoclusters and ZnO graphenelike–nanosheets are within –13.96 to –9.05 kcal/mol for H_2O and –14.11 to –8.39 kcal/mol for NH_3 and all the H_2O and NH_3 adsorptions on ZnO nanoclusters and ZnO graphenelike–nanosheets are not influential their energy gaps.

From literature reviews, it is seen that there was still no research about sensors of gaseous molecules of NH_3 on multiple CNL–ZnO' nanosheets using quantum chemistry calculation with density functional theory in the level of B3LYP/LanL2DZ.

Results and Discussion

1. Adsorption of ammonia molecule

The B3LYP/LanL2DZ–optimized structures of adsorption configurations of NH_3 on single– and multi–layer CNL–ZnONS's are shown in Figure 1 and their adsorption energies are shown in Table 1. The adsorption configurations of NH_3 adsorption on the single–, double–, triple– and quadruple–layer CNL–ZnONS's are composed of two configurations for each. All adsorption configurations are non–dissociative adsorption except one of the NH_3 on the single–layer CNL–ZnON'S which is dissociative. There are two types of NH_3 adsorptions on multi–layer CNL–ZnONS's. One adsorption site is at edge of outer layers and another is in between outer and the next inner layers. The adsorption energies of NH_3 on the edge of outer layer are slightly higher than of the inner layer. Their adsorption energies are within the range of –28.25 to –21.52 kcal/mol.

2. Energy gaps and chemical indices of adsorption complexes with CNL–ZnONS's

The energy gaps, chemical indices and electronic charge transfer of CNL–ZnON'S, of its multiple layers and their adsorption configurations are shown in Table 2. The table shows that all the adsorption configurations of NH_3 on single– and multiple–layer CNL–ZnONS's have lower energy gaps compared to bare clusters of their corresponding CNL–ZnONS's. All chemical indices of bare single– and multiple–layer CNL–ZnONS's and their NH_3 configurations are not much difference except NH_3 dissociative adsorption on the single–layer CNL–ZnONS', $H.NH_2$/CNL–ZnONS' (1). Due to $H.NH_2$/CNL–ZnONS' (1) has very low energy gap (E_{gap}=1.318 eV) as compared with its bare CNL–ZnONS' (E_{gap}=3.290 eV), the single–layer CNL–ZnONS' may be applied as NH_3 sensor.

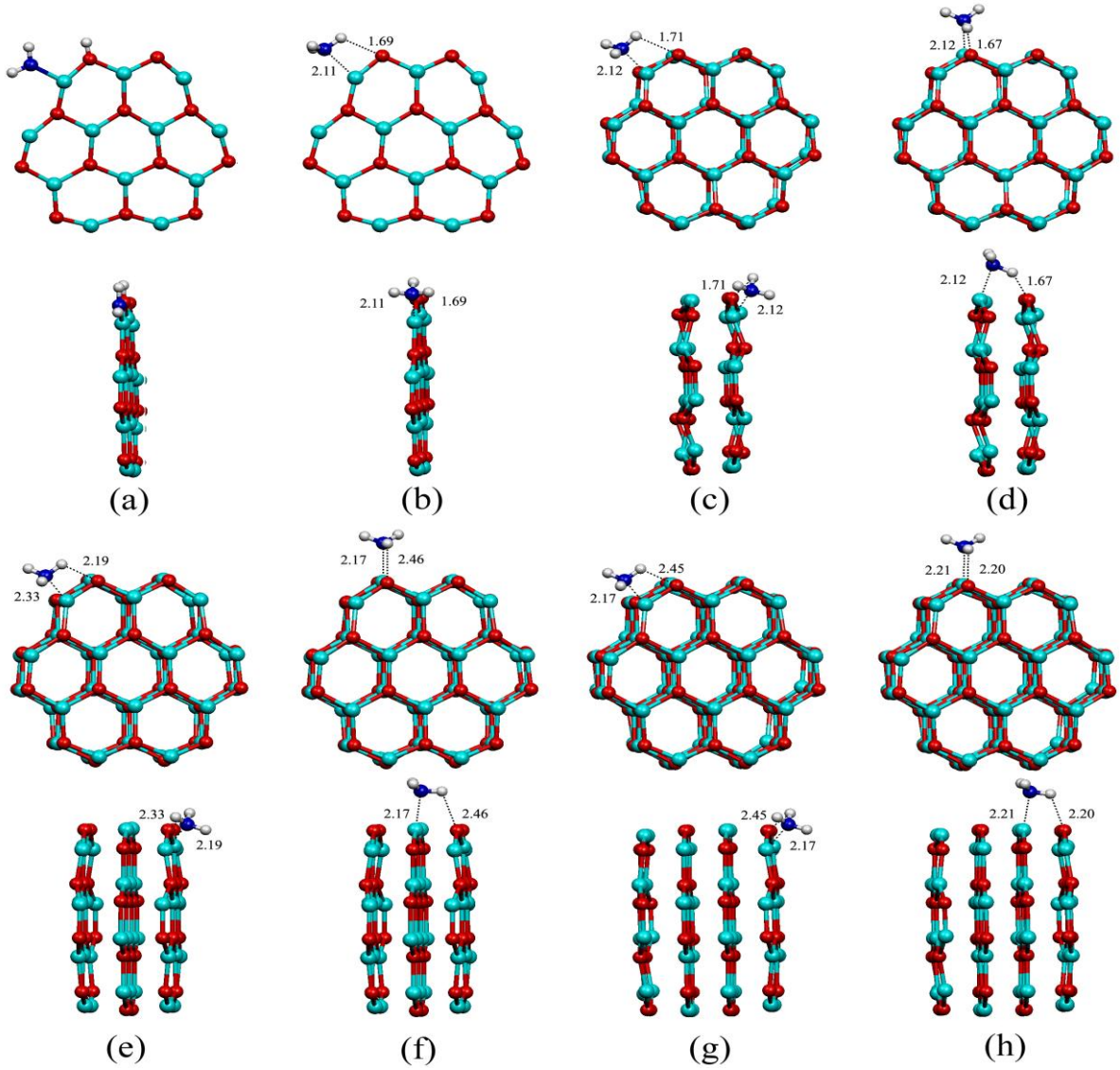

Figure 1 B3LYP/LanL2DZ–optimized structures of ammonia adsorption on CNL–ZnONS's as (a) $H.NH_2$/CNL–ZnONS' (1), (b) NH_3/CNL–ZnONS' (2), (c) NH_3/$(CNL–ZnONS')_2$ (1), (d) NH_3/$(CNL–ZnONS')_2$ (2), (e) NH_3/$(CNL–ZnONS')_3$ (1), (f) NH_3/$(CNL–ZnONS')_3$ (2), (g) NH_3/$(CNL–ZnONS')_4$ (1) and (h) NH_3/$(CNL–ZnONS')_4$ (2). Top and side views are shown on top and bottom, respectively. Bond distances are in Å.

Table 1 Adsorption energies (ΔE_{ads} in kcal/mol) of NH_3 on CNL–ZnONS' and its multiple sheets, computed at the B3LYP/LanL2DZ level of theory.

Adsorption	ΔE_{ads}
NH_3 adsorbate	
Single layer cluster:	
NH_3 + CNL–ZnONS' ⟶ H.NH_2/CNL–ZnONS' (1)	–21.52
NH_3 + CNL–ZnONS' ⟶ NH_3/CNL–ZnONS' (2)	–28.25
Double layer cluster:	
NH_3 + (CNL–ZnONS')$_2$ ⟶ NH_3/(CNL–ZnONS')$_2$ (1)	–27.86
NH_3 + (CNL–ZnONS')$_2$ ⟶ NH_3/(CNL–ZnONS')$_2$ (2)	–24.54
Triple layer cluster:	
NH_3 + (CNL–ZnONS')$_3$ ⟶ NH_3/(CNL–ZnONS')$_3$ (1)	–27.25
NH_3 + (CNL–ZnONS')$_3$ ⟶ NH_3/(CNL–ZnONS')$_3$ (2)	–22.18
Quadruple *layer cluster:*	
NH_3 + (CNL–ZnONS')$_4$ ⟶ NH_3/(CNL–ZnONS')$_4$ (1)	–28.25
NH_3 + (CNL–ZnONS')$_4$ ⟶ NH_3/(CNL–ZnONS')$_4$ (2)	–21.59

Table 2 HOMO–LUMO gaps (E_{gap}), chemical indices and electronic charge transfer of adsorption configuration of multiple layer CNL–ZnONS' species.

Species	E_{gap} [a]	η [a,b]	S [c]	μ [a,d]	χ [a,e]	ω [a,f]	ΔN_{max} [g]
Bare clusters:							
CNL–ZnONS'	3.290	1.645	0.304	–4.916	1.645	7.345	2.988
$(CNL–ZnONS')_2$	3.447	1.724	0.290	–4.800	1.724	6.683	2.785
$(CNL–ZnONS')_3$	3.210	1.605	0.312	–4.755	1.605	7.042	2.962
$(CNL–ZnONS')_4$	3.300	1.650	0.303	–4.755	1.650	6.851	2.882
NH_3 adsorption							
$H.NH_2$/CNL–ZnONS' (1)	1.318	0.659	0.759	–4.068	0.659	12.561	6.175
NH_3/CNL–ZnONS' (2)	3.044	1.522	0.329	–4.536	1.522	6.759	2.980
$NH_3/(CNL–ZnONS')_2$ (1)	3.298	1.649	0.303	–4.517	1.649	6.185	2.739
$NH_3/(CNL–ZnONS')_2$ (2)	3.145	1.573	0.318	–4.460	1.573	6.325	2.836
$NH_3/(CNL–ZnONS')_3$ (1)	3.115	1.557	0.321	–4.532	1.557	6.595	2.910
$NH_3/(CNL–ZnONS')_3$ (2)	3.031	1.516	0.330	–4.528	1.516	6.764	2.988
$NH_3/(CNL–ZnONS')_4$ (1)	3.206	1.603	0.312	–4.558	1.603	6.480	2.843
$NH_3/(CNL–ZnONS')_4$ (2)	3.204	1.602	0.312	–4.595	1.602	6.588	2.868

[a] In eV.

[b] Chemical hardness, $\eta = E_{gap}/2$.

[c] Chemical softness, $S = 1/E_{gap}$, in eV^{-1}.

[d] Electronic chemical potential, $\mu = (E_{HOMO} + E_{LUMO})/2$.

[e] The Mulliken electronegativity, $\chi = -(E_{HOMO} + E_{LUMO})/2$.

[f] The electrophilicity, $\omega = \mu^2/2\eta$.

[g] The maximum electronic charge transfer, $\Delta N_{max} = -\frac{\mu}{\eta}$.

Conclusions

The adsorption configurations of NH_3 adsorption on the single–, double–, triple– and quadruple–layer CNL–ZnONS's are composed of two configurations for each. The chemical indices of bare single– and multiple–layer CNL–ZnONS's and their NH_3 adsorption configurations are not much difference except NH_3 dissociative adsorption on the single–layer CNL–ZnONS', $H.NH_2$/CNL–ZnONS' (1). Due to $H.NH_2$/CNL–ZnONS' (1) has

very low energy gap (E_{gap}=1.318 eV) as compared with its bare CNL–ZnONS' (E_{gap}=3.290 eV), the single–layer CNL–ZnONS' may be applied as NH_3 sensor.

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