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การคำนวณและการศึกษาโครงสร้างทางอิเล็กทรอนิกส์ของ ZnO ที่ถูกเจือด้วยอะตอมของไนโตรเจน

The Electronic Structure of N-doped ZnO Calculated by First Principle Calculation

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บทคัดย่อ

การดัดแปลงโครงสร้างอิเล็กทรอนิกส์ของสารประกอบเป็นวิธีหนึ่งที่สามารถเพิ่มประสิทธิภาพตัวเร่งปฏิกิริยาทางแสงของสารเหล่านั้นได้ ในงานนี้ได้ทำการศึกษาเชิงทฤษฎีของการดัดแปลงโครงสร้างของ ZnO ในการศึกษานี้ได้ทำการคำนวณและศึกษาสมบัติทางโครงสร้างอิเล็กทรอนิกส์ เช่น ความหนาแน่นสถานะ และโครงสร้างแถบพลังงาน ของ ZnO และ ZnO ที่เจือด้วยธาตุไนโตรเจน การคำนวณได้ใช้ทฤษฎีฟังก์ชันนัลความหนาแน่นในโปรแกรม Vienna Ab initio Simulation Package (VASP) ระเบียบวิธีการประมาณแบบ GGA+U ได้ถูกนำมาใช้เพื่ออธิบายพลังงานศักย์สัมพันธ์แลกเปลี่ยนของการจำลอง จากการศึกษาพบว่าโครงสร้างแถบพลังงานของ ZnO ที่เจือด้วยธาตุไนโตรเจนแสดงโครงสร้างทางอิเล็กทรอนิกส์ที่ดี กล่าวคือมีการปรากฏสถานะที่อยู่ใกล้กับแถบวาเลนซ์ และความกว้างของช่องว่างแถบพลังงานมีการลดลงจาก 2.24 eV เป็น 1.92 eV ซึ่งมีความเป็นไปได้ว่า ZnO สามารถทำหน้าที่เป็นตัวเร่งปฏิกิริยาเชิงแสงได้ในช่วงคลื่นแสงที่ตามองเห็นได้ ดังนั้นการเจือไนโตรเจนเข้าไปใน ZnO จะเป็นการเพิ่มประสิทธิภาพการทำงานในเชิงการเป็นตัวเร่งปฏิกริยาเชิงแสงได้ อีกทั้งการเจือไนโตรเจนเข้าไปในโครงสร้างของ ZnO มีผลทำให้แถบเฟอร์มีขยับลงมาใกล้กับแถบวาเลนซ์มากขึ้น ซึ่งมีความเป็นไปได้ว่า ZnO ที่ถูกเจือด้วยไนโตรเจนแสดงสมบัติเป็นสารกึ่งตัวนำชนิด p-type จากการศึกษาของงานนี้จะพบว่าการเจือไนโตรเจนลงในโครงสร้างของ ZnO ส่งผลให้ ZnO มีโครงสร้างอิเล็กทรอนิกส์ที่เปลี่ยนแปลงไปจากเดิมทำให้ ZnO สามารถนำไปประยุกต์ใช้ได้กว้างขวางขึ้น

ABSTRACT

To improve photocatalytic performance of any element or compound, its electronic structure will be modified. In this work, ZnO structure is modified by N doping. Because there are experimental researches reported that N-doped ZnO shows higher photocatalytic activity than pure ZnO. Zinc oxide and nitrogen-doped zinc oxide were calculated and investigated electronic structure via density of states (DOS) and band structures. The calculation was carried out by density functional theory (DFT) using Vienna Ab initio Simulation Package (VASP) code. GGA+U is employed to describe exchange-correlation potential of the simulation. The calculated electronic structure of nitrogen doping in zinc oxide shows appreciate electronic structure, occurring new states at the top of valence band and being narrower of E_g from 2.24 eV of direct band gap to 1.92 eV. Also, p-type characteristic of dopant system is observed from shifting of Fermi level to lower energy near valence states. Being narrower of band gap suggests that ZnO can photocatalytic degrade under visible range. It suggests that N-doped ZnO can improve photocatalytic performance of ZnO. Also, nitrogen doping could turn n-type zinc oxide into p-type material for more applications.

คำสำคัญ: ตัวเร่งปฏิกิริยาเชิงแสง ZnO ที่เจือไนโตรเจน ฟังก์ชันนัลความหนาแน่น

Keywords: Photocatalytic activity, N-doped ZnO, DFT

INTRODUCTION

For a decade ZnO, a non-magnetic, an ecological friendly material and n-type semiconductor with wide direct band gap of 3.37 eV (Aydin et al., 2013), has rigorously attracted research attention for its exceptional properties and resourceful applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors, solar cells (Choi et al., 2015), gas sensors (Vanalakar et al., 2015), varistors (Wang et al., 2014), transistors (Heo et al., 2004). There are three structures of zinc oxide which are a stable hexagonal wurtzite structure, a metastable cubic zinc blende structure, and high pressure rock salt (Haq et al., 2012; 2014). Because the most stable structure at room temperature is wurtzite phase, there are many literatures regarding wurtzite applications.

Besides applications above, ZnO is one of a potential compound which is utilized as photocatalysts in photocatalytic process to water split because it’s low cost, easy to prepare, non-toxic and abundant availability. Also, its energy band gap (E_g) is corresponding to UV range light. Photocatalytic process is utilization from photon energy to chemical process catalyst. Both water splitting and waste water treatment are utilization from the photocatalytic process. In case of waste water treatment, normally, water turbine is employed to treat waste water. Oxygen will be added to the waste water. However, adding oxygen to the waste water isn't enough to solve waste water problem because the waste water consists of a lot of chemical compound such as phosphorus compound. The photocatalytic process can split chemical compound then, these chemical will be separated physically. Firstly, catalysts gain photon energy. If the energy is greater than or equal to E_g of the catalysts, electrons in valence band will hop to conduction band and holes will be left at valence band. Holes react to organic compound and H_2O then, CO_2 as well as H_2O, and hydroxyl radical with hydrogen ion will be obtained, respectively. Also, they can react to phosphorus, nitrogen and other chemical compound. For example, when holes react to phosphorus, the phosphorus ion will be generated. Chemical reaction of hole side is oxidation. In the presence of electrons, electrons will react to oxygen then, superoxide ion radical will be gotten. This reaction's called oxidation. Finally, the hydroxyl radical will react to chemical compound as well. It results in oxygen compound of any element such as CO_2 (for organic compound) and H_2O. For case of other element such as heavy mass metal; Mg, it can be separated from water by hydroxyl radical which it will react to magnesium, resulting in $MgCO_3$ and H_2O. Finally, $MgCO_3$ precipitates will be removed from the water. From the waste water treatment process, we see that much number of carriers will lead photocatalytic process to be high performance. However, if E_g is much narrower, carriers; electrons and holes, will recombine quickly. It results in less photocatalytic activity. So the convenient E_g is required to provide high photocatalytic performance.

UV light, according to E_g of the ZnO, is just 4% of solar spectrum which 43% is visible range (Zong et al., 2013). Thus, being narrower of E_g is expected to improve efficiency of photocatalytic performance. Other researchers reported that N-doped ZnO shows higher photocatalytic activity than pure ZnO. For example, Zong et al. (2013), they reported that the N-doped ZnO can absorb light in wider wave length than the ZnO. When performance of water oxidation under visible light irradiation was measured, the nitrogen-doped ZnO bundle-like nanoparticles shows high performance for water oxidation and higher than the undoped ZnO. In the same direction to Yang et al. (2009), they measured photocurrent generated of the N-doped ZnO compared to the pure ZnO. From their results, the N-doped ZnO generates photocurrent more than the pure ZnO. Both higher performance of water oxidation and photocurrent generated of the N-doped ZnO than the undoped ZnO under UV-Vis light are due to being narrower of E_g. An advantage of the being narrower of E_g, electrons can jump to conduction band easier. If the E_g corresponds to visible range, sample can absorb the photon and hop to conduction band. It results in catalyst can water oxidize under visible light which is more than 40% of solar spectrum. In addition, when NH_3 gas was flowed to ZnO, Das et al. (2015) reported sample shows narrower E_g of 3.17 eV and p-type nature. To more understanding in these results, electronic structure is employed to describe band structure of the pure ZnO and N-doped ZnO. However, N-doped ZnO hasn't been studied widely so the study of electronic structure is still required. Thus, aim of this work is to investigate the electronic structure of N-doped ZnO in theoretical aspect which is simulated using density functional theory (DFT) study.

COMPUTATIONAL DETAILS

First principle calculation of fundamental constant without experimental data were employed in this calculation. The calculation of a system which number of nuclei N and number of atoms k, Schrodinger's equation was solved as

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V^{eff}(\vec{r})\right\}\psi_{n\vec{k}}(\vec{r}) = E\psi_{n\vec{k}}(\vec{r})$$

where $V^{eff}(\vec{r})$ is effective potential. It could be written as

$$V^{eff}(\vec{r}) = V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$$

when $V_{ion}(\vec{r})$ is the potential from the nuclei which is screened by core electrons. In this work, the V_{ion} was described by pseudopotential.

$V_H(\vec{r})$ is the Hartree potential which

$$V_H(\vec{r}) = \frac{e^2}{4\pi\varepsilon_0}\int dr' \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|}.$$

And $V_{xc}(\vec{r})$ is the exchange and correlation potential. The potential of the DFT is defined that it depends on the electron density ($\rho(r)$) which

$$\rho(\vec{r}) = \sum_{n\vec{k}} |\psi_{n\vec{k}}(\vec{r})|^2 .$$

In this calculation, the pure ZnO and N-doped ZnO ($Zn_{1-x}N_xO$) were modeled as ideal hexagonal wurtzite structure with a 2×2×2 super-cell which corresponds to a supercell that was eight times as large as the size of a primitive wurtzite unit cell in base plane direction. In this system, an atom of O was replaced by N atom. The orbitals of N($2s^2 2p^3$), Zn($3d^{10} 4s^2$), and O($2s^2 2p^4$) were treated as valence electrons. The DFT study of the projector augmented wave (PAW) (Blochl, 1994) pseudopotential method was used on the Vienna Ab initio Simulation Package (VASP) software package (Kresse et al., 1996). Generalized Gradient Approximation (GGA+U) with Hubbard model in scheme of Perdew–Burke–Ernzerh (PBE) was used to treat more exchange and correlation energy. Coulomb interaction U_{eff} of Zn as 9.0 eV was employed. A 11×11×11 k-point mesh in the Brillouin zone was employed and the cutoff energy of the plane wave is 400 eV.

RESULTS AND DISCUSSION

In this work, the 32 atoms of optimized systems of both zinc oxide and nitrogen-doped zinc oxide structures were simulated by first principle calculation as shown in Fig. 1. An atom of nitrogen was added into zinc oxide structure as shown in Fig. 1 (b).

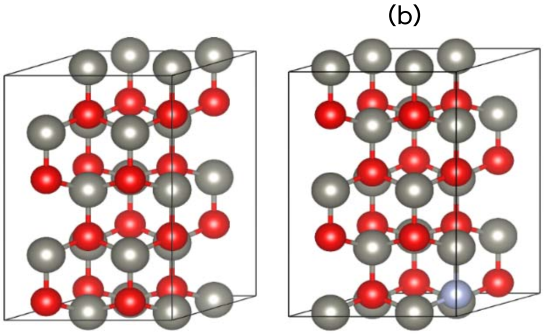

Fig. 1 Simulated structures of (a) zinc oxide and (b) nitrogen-doped zinc oxide with gray ball of the zinc, red the oxygen and, blue the nitrogen atoms

To investigate electronic structure of both ZnO and N-doped ZnO, density of states (DOS) and band structures were calculated. Firstly, the DOS as shown in Fig. 2 will be considered. Fermi level is at 1.3739 eV for pure ZnO and 1.2311 eV for N-doped ZnO system. When we compare Fig. 2(a) of pure ZnO to (b) of dopant system, we see that there are new states at the top of valence band in the nitrogen-doped zinc oxide system. These new states might be due to interaction of nitrogen atom to zinc and oxygen atoms according to calculated results of Sha et al. (Sha et al., 2015). For the new states, electrons in this state can jump to conduction band more easily than the pure zinc oxide. It results in more number of carriers generated. In case of photocatalytic process, number of generated carriers bring about increasing of photocatalytic performance.

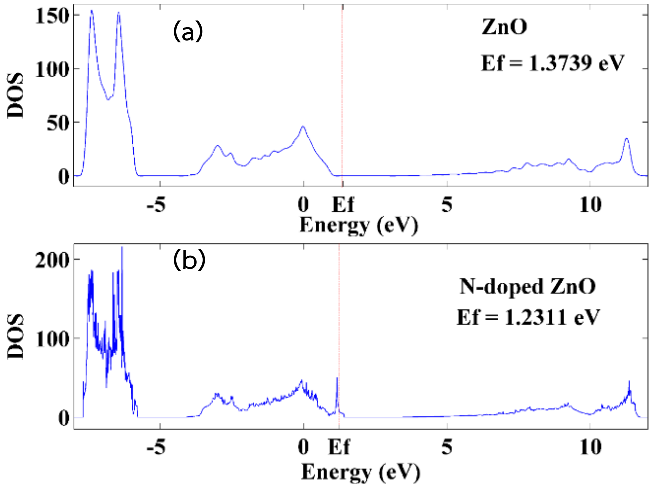

Fig. 2 Total density of states of (a) undoped ZnO and (b) N-doped ZnO with dash line of Fermi level locating at 1.3739 and 1.2311 eV for pure and N-doped ZnO, respectively

Next, calculated band structure of zinc oxide and N-doped ZnO which the x-axis of wave vector and the y axis of energy were plotted and represented in Fig. 3. The Fermi level is at 1.4209 and 1.3489 eV for pure and N-doped ZnO, respectively. Energy band gap of ZnO is 2.24 eV. A very being narrower of E_g comparing to experimental result (3.37 eV) is resulting from weak interaction of electrons. Because of in this calculation, potential of particles was approximated by DFT. Underestimating of band gap of the calculated result than the experimental result is due to the limit of the DFT calculation. This system is direct band gap because maximum energy of valence band and minimum energy of conduction band is at the same wave vector of zero (Gamma point, G). In case of dopant system, E_g is about 1.92 eV. Being narrower of E_g in the dopant system is due to the new states at top of valence band induced by N-doping according to calculated results of Yu et al. (2016) using CASTEP code. The narrow E_g, when nitrogen was doped on zinc oxide structure, is also observed in experimental results reported by Cheng et al. (2015) and Macías-Sánchez et al. (2015). Besides, being closed to valence states of Fermi level from the DOS of N-doped ZnO is confirmed by the calculated band structure. This result points out that it's possible that N-doped ZnO shows p-type characteristic because Fermi level of dopant system shifts to lower states near valence band comparing to the pure system. This result is according to report of Das et al. (2015). From these results, we see that ZnO can absorb visible light when oxygen atom was replaced by nitrogen atom although pure ZnO could absorb UV range. Also, n-type characteristic of ZnO could turn into p-type when nitrogen was doped on ZnO structure. Therefore, N doping on ZnO structure is a promising material to be applied in various and wider applications.

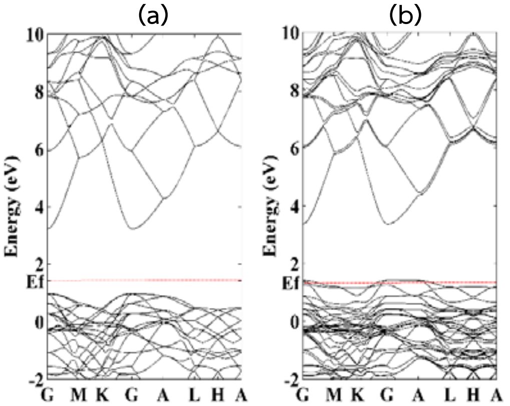

Fig. 3 Band structures of (a) pure ZnO and (b) N-doped ZnO with dash line of Fermi level locating at 1.4209 and 1.3489 eV for pure and N-doped ZnO, respectively

CONCLUSIONS

Electronic structures of undoped ZnO and an atom of N doping on ZnO structure were calculated using DFT via VASP code with GGA+U in the scheme of PBE. From DOS and band structures, new states induced by nitrogen doping at the top of valence band are observed. It results in narrower energy band gap of dopant system than the pure ZnO. The being narrower energy of band gap indicates that nitrogen doping could lead zinc oxide to absorb visible light which will improve photocatalytic performance. Besides, shifting of Fermi level to lower energy closed to valence band of nitrogen-doped zinc oxide system suggests that n-type characteristic of zinc oxide might be turned into p-type by nitrogen doping. Actually, appreciated electronic structure of nitrogen doping will lead ZnO to be applied in more fields than currently possible.

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