Ain-Shams University
Faculty of Science
Chemistry Department

Band Structure Engineering of Metal Oxynitride Semiconductors for Enhanced Photoelectrochemical Water Splitting

A Thesis in Chemistry

By

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Tamer S. El-Shazly
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Abstract

In this work, we reported quantum chemical computations on some metal oxides and their oxynitrides counter parts in quest for engineering their bandgaps and band edges positions. Our goal was to fine-tune the bandgap for driving the water splitting reactions (1.23: 2.2 eV) and bandgap edges to be proper with water splitting potentials. The studies have been carried out performing DFT calculations using the standard CASTEP package implemented in Material Studio version 6. One of the group 5 metal oxide and its metal oxynitride counterpart (B-Nb_2O_5 and NbON) have been targeted for this work.

In the first part of the thesis, the electronic and optical properties of monoclinic Niobium pentoxide (B-Nb_2O_5) belongs to 2/m (B112/B) space group have been studied through studying the doping effects. Two types of dopant been implemented to achieve the targets:

(i): The first dopant was Tungsten (W), the bandgap of B-Nb_2O_5 (3.45 eV) can be significantly tuned into 1.39 eV. The W 5d orbitals affected the position of CBM with negligible effect on VBM. The calculated bandgaps of the B-Nb_2O_5: W showed a bowing phenomenon. Further, the optical dielectric function showed an increased electronic contribution of the dielectric constant at high W content, while the absorption spectrum and refractive index pointes out a red-shift and cladding behaviors, respectively.

(ii): The second dopant was Fluorine (F), the band calculations revealed that B-Nb_2O_5:F is indirect bandgap semiconductor 2.28 eV, the Fermi-level shifts towards the conduction band, allowing optical absorption in the visible region with enhanced transmittance in the wavelength range 400-1000 nm. The effective mass of free charge carriers increased upon F-incorporation.

In the second part, super crystal of NbON monoclinic symmetry with space group $P2_1/c$ have been studied. The electronic and optical properties been computed with varying the N/O ratio. The band calculations revealed that the studied systems are indirect bandgap semiconductors. Varying N/O ratio leads to reallocate the band edges allowing red and blue shift absorption for higher N/O and lower N/O respectively. The dielectric constant and refractive index of pristine NbON are comparable to the experimental values of TaON.

Dedication

(قُلْ إِنَّ صَلَاتِي وَنُسُكِي وَمَحْيَايَ وَمَمَاتِي لِلَّهِ رَبِّ الْعَالَمِينَ)

“Verily, my Salat (prayer), my sacrifice, my living, and my dying are for Allah, the Lord of the 'Alamin (mankind)”

The Noble Qur’an, Surat Al - An'am, Verse [126]

Table of Content

Acknowledgements……. i
Abstract…… ii
Dedication…… iii
List of Figures…….. vii
List of Tables……... x
List of Abbreviations……... Xi

Chapter 1 Introduction……. 1

1-1 Energy Challenge……. 1
1-2 Energy and Chemistry: ENERCHEM……... 2
1-3 Water Splitting……..... 5
1-3-1 Hydrogen Fuel……..... 5
1-3-2 Hydrogen from solar water splitting……... 7
1-3-3 Photoelectrolysis Mechanism…….... 8
1-4 Photocatalytic Materials…….... 11
1-4-1 Binary Oxides…….... 11
1-4-2 Multi Cations Oxides…… 12
1-5 Nb-based Materials for PEC applications……. 13
1-5-1 Niobium pentoxide (Nb_2O_5)……..... 17
1-5-2 Niobium oxynitride (NbON)…… 21
1-6 Crystal structure and electronic properties prediction…….. 23
References……. 26

Chapter 2 Theoretical Background…….…… 37

2-1 General Background……. 38
2-2 Hartree-Fock Self-Consistent Field Method……..... 39
2-3 Post- Hartree-Fock Methods…….. 40
2-4 Density Functional Theory…….. 40
2-4-1 Local density Approximation (LDA)……... 42
2-4-2 Generalized Gradient Approximation (GGA)…….. 43
2-4-3 Types of GGA functionals……. 45
Perdew-Wang 1991 (PW91)……..... 45
Perdew, Burke and Ernzerhof (PBE) …… 46
Revised PBE (RPBE)……..... 46
Perdew, Burke and Ernzerhof for Solids (PBEsol)……..... 47
2-5 Plane Wave Pseudopotential Method…… 48
2-5-1 Plane Wave Basis Set……... 49
2-5-2 Monkhorst-Pack Grids…….. 50
2-5-3 Pseudopotential……. 51
2-5-4 Projector Augmented Wave (PAW)……. 52
2-6 HF/DFT Hybrid Functionals……. 53

2-6-1 Basis Set Terminology…….. 53
Slater Type Orbitals…….. 54
Gaussian Type Orbitals……. 54
Minimal Basis Set……. 55
Split Valence Basis Set……. 55
Polarized Basis Set…… 56
Diffuse Functions……. 56
Effective Core potential……..... 56
2-7 Optical Properties of Periodic Solid Systems……... 57
2-8 Computational Chemistry Platforms……. 58
2-8-1 Common software systems…… 58
2-8-2 CASTEP Package…… 63
2-8-2-1 Advantages, input and output of CASTEP…… 63
Ease of use and input file setup…….. 63
CASTEP capabilities (range of applications)…… 64
2-8-2-2 Parameters indirectly obtained from CASTEP output files…….. 65
Charge carriers concentration…… 65
Electrons and holes effective masses…… 65
References…….**.....** 67

Chapter 3 Results and discussions of Band Structure Engineering of Monoclinic Niobium Pentoxide B-Nb_2O_5..... 84

3-1 Electronic and Optical properties of B-Nb_2O_5 and Nb-W-O systems……. …. 84
3-1-1 Introduction…….. 84
3-1-2 Computational details……... 86
3-1-3 Targeted systems of Nb-W-O…… 87
3-1-4 Results and discussions……. 88
Structural Properties…….. 88
Band structure and bandgap bowing……. 93
Density of States…… 96
Optical Properties……. 98
3-2 Electronic and Optical Properties of Fluorine- doped Monoclinic Niobium Pentoxide (B-Nb_2O_5: F)…… 103
3-2-1 Introduction…….. 103
3-2-2 Computational details……... 104
3-2-3 Results and discussions……. 104
Electronic and band structure calculations……..... 104
Optical properties…..……. 109
References…… 113

Chapter 4 Results and discussions of electronic and optical properties of Niobium Oxynitride varying N/O ratio…….……..... 120

4-1 Introduction…….. 120

4-2 Computational details……..... 121
4-3 Targeted NbON systems……..... 123
4-4 Results and discussions…… 124
Electronic and band structure calculations…… 124
Density of states and charge carriers…… 126
Optical properties…….. 129
References…… 136

Chapter 5 Conclusions and future directions…… 143

5-1 Conclusions and summary…… 143
5-2 Future directions……..... 145
References…… 147
Published Work…… 148
الملخص العربي……..... أ
المختصر العربي…….. ج

List of Figures

Figure 1-1: The terawatt renewable energy challenge……. 2

Figure 1-2: ENERCHEM defines the multiple contributions of chemistry against the challenges of energy ……..… 3

Figure 1-3: Principle of water splitting for hydrogen and oxygen generation…… 5

Figure 1-4: The "hydrogen economy" both of hydrogen sources and usages in energy-related applications…….. 6

Figure 1-5: n-type photoanode Band structure of water splitting device, (a) Illustrate the various processes of photon irradiation, charge transport, electron–hole pair formation and surface reactions, (b) Illustrate the energetic requirements for the minimum thermodynamic energy to split water, photovoltage and catalytic overpotentials for the OER and HER half-reactions……... 7

Figure 1-6: The PEC energetic diagram (metallic electrode and *n*-type semiconductor photoanode). (a): Initial conditions prior contacts, (b): In dark equilibrium after contact, (c): After illumination, and (d): illumination with applied bias [18]…….. 9

Figure 1-7: The band diagram of some metal oxide semiconductors…….. 12

Figure 1-8: Niobium-Oxygen phase diagram…….. 14

Figure 1-9: **Figure 1-9:** The illustration of niobium oxygen systems: some of the main oxides, some of the related electrical and structural characteristics [35, 37, 43-52]; the structure pictures are depicted from http://www.webelements.com..... 16

Figure 1-10. XRD patterns of products of the reaction between $NbOCl_3$ and NH_3 at temperature ranges from 500 to 800 ˚C ……..…. 22

Figure 1-11: Schematic bandgap structure of metal oxynitride (reduced bandgap) with its counterpart of metal oxide (wide bandgap)……. 23

Figure 2.1: A schematic chart to illustrate all-electron showed by the dashed line and pseudopotentials illustrated as solid line and their corresponding wave functions [57]……..…… 52

Figure 3-1: (a) B- Nb_2O_5 crystal structure with space group 2/m (B112/B) as quoted from [31], (b) Nb-W-O of 12.5% W contents, (c) Nb-W-O of 25% W contents, (d) Nb-W-O of 37.5% W contents and (d) Nb-W-O of 50% W contents. Oxygen atoms are in red color, Nb atoms are blue and tungsten atoms W atoms are green…….. 87

Figure 3-2: Pristine Band structure using: (a) PBE, (b) PBEsol and (c) RPBE Exchange correlations.. 93

Figure 3-3: RPBE Band structure of (a) pristine, (b) 12.5% W-doped, (c) 25% W-doped, (d) 37.5% W- doped and (e) 50% W-doped B-Nb_2O_5……. 94

Figure 3-4: Staggered bandgap energy diagram illustrating the charge carrier transport in Nb-W-O… 96

Figure 3-5: (a) Partial and (b) total density of states in pristine Nb_2O_5, (c) total density of states in pristine and Nb-W-O, and (d) partial density of states due to W 5d for different W doping ratios…….. 97

Figure 3-6:(a) Real part $\varepsilon_1(\omega)$ and (b) imaginary part $\varepsilon_2(\omega)$ of the dielectric function$\varepsilon(\omega)$ of pristine and Nb-W-O crystals ……... 99

Figure 3-7. Absorption spectra $\alpha(\omega)$ of pristine and Nb-W-O crystals, (a) versus wave length (nm), (b) versus Energy (eV)……... 100

Figure 3-8: Reflectivity $R(\omega)$spectra of pristine and Nb-W-O crystals …… 101

Figure 3-9: Refractive index of pristine and Nb-W-O crystals, (a) Real part $n(\omega)$, (b) Imaginary part $k(\omega)$……..... 102

Figure 3-10: Crystal structure of (a) B-Nb_2O_5 and (b) B-Nb_2O_5:F, (Nb: Blue, O: Red, F: Green) …..... 105

Figure 3-11: Band structure of (a) B-Nb_2O_5 and (b) B-Nb_2O_5:F……..... 106

Figure 3-12: Partial density of states (a) Nb of B-Nb_2O_5 , (b) O of B-Nb_2O_5, (c) F of B-Nb_2O_5:F, (d) Total density of states of B-Nb_2O_5 and B-Nb_2O_5:F (e) Partial density of states of F-p orbital…… 108

Figure 3-13: Optical properties of the B-Nb_2O_5 and B-Nb_2O_5: F, (a), (b) Real and Imaginary parts of dielectric, (c) Absorption spectrum, (d) Reflectivity spectrum, (e) Transmittance spectrum, (f) and (g) Real and Imaginary parts of refractive index…….. 110

Figure 4-1: the NbON targeted systems, single and super crystals 2x2x1 varying N/O ratio, (Oxygen atoms are in red color, Nitrogen atoms are in dark blue, Nb atoms are in light blue)……. 123

Figure 4-2: Electronic Band structure of (a) $Nb_{16}O_{16}N_{16}$, (b) $Nb_{16}O_{15}N_{17}$, (c) $Nb_{16}O_{14}N_{18}$, (d) $Nb_{16}O_{17}N_{15}$ and (e) $Nb_{16}O_{18}N_{14}$..... 125

Figure 4-3a: Total and partial density of states of pristine super crystal $Nb_{16}O_{16}N_{16}$..... 127

Figure 4-3b: Total density of states (TDOS) of the studied systems…….. 128

Figure 4-3c: PDOS N 2p, O 2p and Nb 4d of $Nb_{16}O_{16}N_{16}$, $Nb_{16}O_{15}N_{17}$, $Nb_{16}O_{14}N_{18}$, $Nb_{16}O_{17}N_{15}$ and $Nb_{16}O_{18}N_{14}$ 129

Figure 4-4: Dielectric constant of the studied systems, (a) Imaginary part, (b) Real part..... 131

Figure 4-5a: Absorption Spectra of the studied NbON systems..... 132

Figure 4-5b: Reflectivity Spectra of the studied NbON systems. 133

Figure 4-5c: Real and Imaginary parts of Refractive index of the studied NbON systems…… 134

Figure 5-1: Phlogopite and Muscovite Structures of Mica……. 145

List of Tables

Table 1-1: The Structure properties of the different Nb_2O_5 phases [62-70]……. 18

Table 3-1: Lattice parameters of B-Nb_2O_5, space group 2/m (B112/B)…… 88

Table 3-2: Detailed Mulliken charges of pristine and W-doped B-Nb_2O_5 crystals…….. 89

Table 3-3: Average Mulliken charges of pristine and W-doped B-Nb_2O_5 crystals…….. 92

Table 3-4: Mulliken charge, bandgap (eV) and the effective mass of B-Nb_2O_5 and B-Nb_2O_5:F.. 107

Table 4-1: Average Mulliken charges, electron and hole effective mass of the studied NbON system……. 124

Table 4-2**:** Electron and hole effective mass of the studied systems……... 128

List of abbreviations

T	Absolute temperature
$Y_{l,m}$	Angular momentum
BHH	Becke's half-and-half
B3	Becke's three parameter mixing of exchange
k_B	Boltzmann constant
CI	Configuration Interaction
E_J	Coulomb energy,
CC	Coupled Cluster theory
DFT	Density functional theory
ECPs	Effective core potentials
eV	electron volt
E_g	Energy gap
E_{XC}	exchange correlation term
FE	Fermi Energy
FMO	Frontier molecular orbitals
GTOs	Gaussian Type Orbitals
GGA	Generalized gradient corrected Approximation
$\hat{H}$	Hamiltonian operator
HF	Hartree- Fock
HOMO	Highest occupied molecular orbital
IE	Ionization energy
T_s	kinetic energy
KS	Kohn-Sham
LYP	Lee-Yang-Parr
LCAO- MO	Linear-combination of atomic orbitals to form molecular orbitals
LDA	Local density approximation
LSDA	Local Spin Density Approximation
LANL2DZ	Los Alamos National Laboratory Double Zeta
LUMO	Lowest unoccupied molecular orbital

MPn	Møller-Plesset perturbation theory
MCSCF	Multi-Configuration Self Consistent Field
N	Normalization constant
E_{ne}	Nucleus-electron interaction energy
ζ	orbital exponent
OLED	Organic light emitting diod
P86	Perdew 86
PW91	Perdew and Wang
PBE	Perdew, Burke and Ernzerhof
RPBE	Revised Perdew, Burke and Ernzerhof
PBEsol	Perdew, Burke and Ernzerhof for solids
n, l and m	principle, angular momentum and magnetic quantum numbers
STOs	Slater Type Orbitals
r, θ and ϕ	spherical coordinates
VWN	Vosko, Wilk and Nusair
WFT	Wave functional theory
Ψ	Wave function
CBM	Conduction Band Minimum
VBM	Valence Band Maximum
TDOS	Total Density of States
PDOS	Partial Density of States
MOCVD	Metal-Organic Chemical Vapour Deposition
PEC	Photoelectrochemical device
CASTEP	Cambridge Serial Total Energy Package
$\varepsilon_1(\omega)$	Dielectric real part
$\varepsilon_2(\omega)$	Dielectric Imaginary part
$\alpha(\omega)$	Absorption spectrum
$R(\omega)$	Reflectivity
$n(\omega)$	Real part Refractive index
$k(\omega)$	Imaginary part Refractive index