Ab initio molecular dynamics and DFT calculations as support tool and predecessor to experimental investigations of new energy materials

A Thesis

Submitted

By

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Dedicated to

my teachers

and

family

Declaration by the Research Scholar

This is to certify that the thesis titled "**Ab initio molecular dynamics and DFT calculations as support tool and predecessor to experimental investigations of new energy materials**" submitted by me, to the Indian Institute of Technology Mandi for the award of the degree of **Master of Science (by research)**, is a bona fide record of the research work carried out by me in the School of Engineering, Indian Institute of Technology Mandi, under the supervision of Dr. Rahul Vaish. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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Thesis Certificate

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Preamble

The idea envisaged back in 1959, in a popular talk by Richard P. Feynman, “There's Plenty of Room at the Bottom”, introduced the world to nanotechnology. Since then, with the vision of “manoeuvring things atom by atom”, much has been explored at fundamental level of condensed matter. Scanning tunnelling microscope (STM), atomic force microscope (AFM), lithography, ambient pressure photo-electron spectroscopy (APSS) are some of the major milestones achieved in this regard. These tools have allowed us to explore atoms and molecules in their native state, as the building blocks of this world. This has provided us with new insight into an unforeseen domain regarding the actual behavior of atoms and molecules. Nevertheless, this advancement is very recent when compared to the most primitive and effective tool for material analysis: the computational simulation techniques. Sophisticated instrumentation has only served as a supporting tool for corroborating and seldom correcting what have already been predicted using computational tools such as density functional theory, first principles analysis and molecular dynamics. However, such attempts were extremely limited with respect to their accuracy and depth of perception owing to the limited computational power available for earlier works. Nevertheless, with the advent of powerful computers, *ab initio* methods and calculations revolutionized the domain of realistic computational simulations. This was made possible by pushing the limits of consolidated classical molecular dynamics and quantum theory approach. Often referred to as the “virtual laboratory” these methods now find their widespread applications in physics, chemistry, and more recently in biology as well. Further, they serve as an important precursor to many experimental approaches and provide valuable insight into phenomenon which is difficult to quantify through physical means. In the words of J.M. Hailey, "Science has its fashion, just as do literature and music and architecture". In the same regards, with the progress of computational power, the field matured and it transcended the prevalent techniques used in the classical simulations.

Amidst the list of potential methods, in the realms of computational chemistry, this thesis attempts to explore and utilize *ab initio* molecular dynamics and density functional theory (DFT) as both a support tool and an experimental predecessor, for property prediction for

hybrid/advanced composites. This has been demonstrated through dedicated case-studies. The classical simulations theory has been employed for development of new materials which could serve as potential candidates for latent heat storage systems. Quantum theory based simulation techniques have been used to determine the microscopic mechanism occurring in the catalytic materials, developed for environmental detoxification.

The results obtained in the present investigations have been compiled as five chapters as follows:

Chapter 1 attempts to make a comprehensive introduction to the computational techniques employed in this study. Their general history, advantages and limitations and underlying phenomenon has been discussed. Further, the relevant case studies have been mentioned with reasons pertinent to their selection and the specific tools employed for the same.

Chapter 2 deals with first case study where *ab initio* molecular dynamics simulations have been carried out to investigate the phase transition behavior of n-docosane with carbon nano-additives. Classical molecular dynamics have assisted in elucidation of thermal average potential, kinetic and non-bond energy with the varying percentage of nanofillers. Crucial thermo-physical attributes have been determined, which could serve as precursor to experimental investigations.

Chapter 3 expands on the previous study, by considering more promising carbon nano-additives in order to address the thermal conductivity issue in paraffin hydrocarbons. Insights were revealed into self-diffusion coefficient and overall energy of the composite. The investigations indicated that an optimum composition, corresponding to the best latent heat storage system could be determined through meticulous analysis of the microscopic properties. The proposed methodology could assist in circumventing the experimental route that involves numerous iterations to determine the optimum loading of carbon nanofillers.

Chapter 4 deals with the implementation of DFT to elucidate the molecular orbital contribution with respect to the catalytic activity of $BaTiO_3$-reduced graphene oxide composites. The proposed approach and study aided in assimilation of transport characteristics of charge carriers from valence states to conduction states; engaged in various oxidation processes. Additionally, it also assisted in corroborating the

experimental results as obtained from DRS(diffuse reflectance spectroscopy). The surface orientation of $BaTiO_3$ particles over the stacked layer of reduced graphene oxide could also be elucidated by employing the DFT calculations.

Thesis ends with summary and conclusions, though each chapter is provided with its own set of conclusions. The following publications are largely based on the studies conducted as a part of the research work reported over here.

1. ***Monisha Rastogi***, Aditya Chauhan, Rahul Vaish and Anil Kishan," Selection and performance assessment of phase change materials for heating, ventilation and air-conditioning applications *"Energy Conversion and Management*, Elsevier 89, 260 (2015).
2. ***Monisha Rastogi*** and Rahul Vaish, "Molecular dynamics insight to phase transition in nalkanes with carbon nanofillers" *AIP Advances* 5(124):57141-154706 ,(2015).
3. ***Monisha Rastogi***, H.S Kushwaha and Rahul Vaish "Highly efficient visible light mediated azo dye degradation through barium titanate decorated reduced graphene oxide sheets" *Electronic Materials Letter*, Springer (accepted), (2015).
4. ***Monisha Rastogi***, Chris Bowen , Aditya Chauhan ,H.S. Kushwaha and Rahul Vaish "Experimental and first principles insights into barium titanate clusters decorated graphene sheets: Heterogeneous catalysis and advanced oxidation processes". (under review), (2015).
5. ***Monisha Rastogi***, Rahul Vaish, Niyaz Ahmad Madhar, Hamid Shaikh and S. M. Al-Zahrani " Rational molecular dynamics scheme for predicting optimum concentration loading of nano-additive in phase change materials". AIP Advances 5, 107240 (2015).

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