IJTA

International Journal of Therapeutic Applications
ISSN 2320-138X

QUANTUM CHEMICAL CORRELATION OF HOMO-LUMO GAP AND ADSORPTION ENERGY OF ZnO AND ZnS

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ABSTRACT

The study focuses to understand the correlation between adsorption energy and band gap of nanoparticles like ZnO and ZnS during their adsorption onto biological systems. Simulated annealing and semi-empirical pm3 methods were applied using computational chemistry software HyperChem. The results of this experiment demonstrated that there exists a relationship between hydrogen adsorption, hydrogen bonding and energy band gap which would in turn be useful for developing promising nano medicines. This gains immense importance due to the growing need of nano medicines and nano bio-sensors due to their nano dimensions.

Keywords: nanomedicines, hydrogen adsorption, semiemperical pm3, band gap, ZnO and ZnS nanoparticles

INTRODUCTION

Nano particles due to their unique dimensions have found to possess unique physio-chemical properties. Due to these unique properties they play a vital role in the biological process especially in the human body at the cellular level. Emergence of various fields like nano medicine, nano diagnostic tools and biosensors are an outcome due to the immense strides achieved in the field of nanotechnology [1-6]. Thus revolutionizing the way in which we think, detect and treat a disease.

Metals like zinc play a crucial role in several biological processes, proteins and functioning of muscle[7]. Their nano particles like ZnO, ZnS and ZnSe have been found to possess therapeutic, conducting and semi-conducting properties[2] as well. Other applications like development of new pharmaceutical preparations, anti-inflammatory and reparation action in treating experimental wounds, selective destruction of cancer cells and identification of proteins present in blood serum of human body[8,9] have shown that there may exist certain adhesive like hydrogen interactions that are responsible for the biological activity of the known compounds.

Weak bonding interactions such as hydrogen bonding, electrostatic interaction, vander Waals interactions all play a significant role during adsorption processes[10-13] on to biological systems as well as in band gap energy calculation in semiconductors; our study focused on whether there exists any correlation between band gap energies and adsorption that where calculated insilico.

MATERIALS AND METHODS

The studies were conducted insilico using

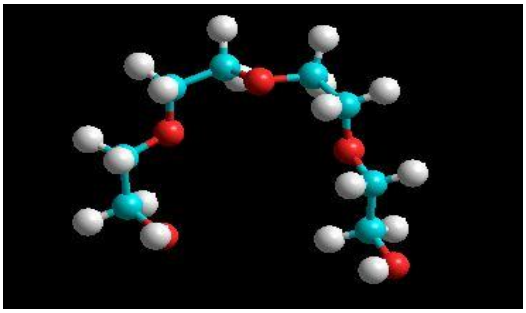

Fig:1 PEG polymer

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computational chemistry package HyperChem® Release 8 for Windows[14]. Created glycol polymer chain (*Polyether poly(ethylene glycol)).* As PEG **(Fig:1)** can solubilize hydrophobic drugs due to its high hydrophiliity, thereby minimizing the interaction with the immune system thus helping in extending the circulation of compounds resulting in an effective mechanism of drug delivery to the target organs[15]. Energy minimizations of the structure were done using molecular mechanics OPLS method[16]**.** Global minimum were calculated through simulated annealing by varying the temperature from 300K to 2000K[17]**.** Geometry optimized to low energy structure using PM3 semi empirical method at the Restricted Hartree Fock (RHF) level. Different cluster sizes of ZnO and ZnS nano crystals were created by

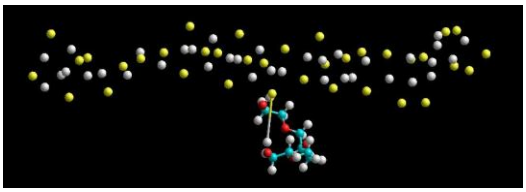

Fig:2 PEG with adsorbed ZnS nanomolecule with 36 units.

cutting it in the HyperChem space and crystals with 12, 18,24,30,36 zinc oxide units and zinc sulfide units were created. Geometry optimization of these nanoparticles were done using semi empirical PM3 method. The HOMO-LUMO band gap had been estimated. Capping of nanocrystal with polymer was done using file-merge command, and then merged the PEG molecule with the nanocrystal. After which deleted hydrogen from the PEG molecule and added one hydrogen to one of oxygen's that was at a distance 0.96A° on nanoparticle surface. Geometry optimization was done for the merged molecular system using semi empirical PM3 method(**Fig:2 and 3**).

Finally to calculate the adsorption energy , following formula was used.

Adsorption energy E = [E (molecule) + E (nanoparticle)] – [E (merged system)]

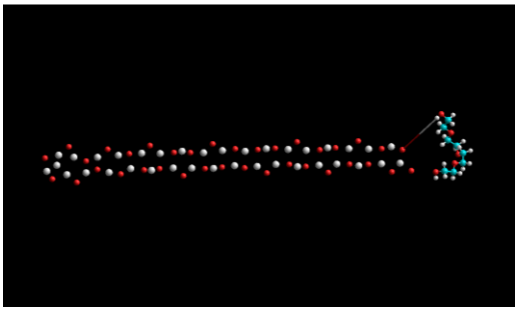

Fig:3 PEG with adsorbed ZnO nanomolecule with 36 units

RESULTS AND DISCUSSION

From Table:1 and Table:2 , it is evident that the energy of the structure capped with PEG polymer were calculated through optimization and it was found that the energy of the system decreases with increase in cluster size. The adsorption energy of hydrogen on the nano ZnO and ZnS surface depends on the size of the nano crystal. The adsorption energy was least for ZnO with 24 units , ZnS with 36 units. It was found that the band gap trends are similar for both ZnO and ZnS . There lies similar trend between adsorption energy and band gap of the merged system (Fig:4 and 5). It is clearly mentioned in literature that tunable band gap by controlling the adsorption coverage on nano materials such as nanomedicine and nanoelectronics gaining popularity as it would be useful in the designing of nanomaterial with desired properties of our interest[18-20].

The outcome of this study in which the band gap

Table:1 Energy of the nano ZnO capped with PEG polymer

No.of ZnO Units	E-ZnO	Band gap	E-polymer	E-merged	Adsorp-tion n energy	HOMO-merged	LUMO-merged	Band gap
12	-1134.6297	5.5751	-2815.7686	-4046.7829	96.3846	-10.2875	-3.5838	6.7037
18	-1708.1138	5.8604	-2815.7686	-4525.6251	1.7427	-10.5204	-5.0482	5.4722
24	-2301.7448	5.8136	-2815.7686	-5117.2107	-0.3027	-10.5361	-5.1081	5.428
30	-2912.6212	5.8495	-2815.7686	-5823.2913	94.9015	-10.1692	-4.334	5.8352
36	-3513.8007	5.8247	-2815.7686	-6334.3152	4.7459	-10.5842	-4.9986	5.5856

Table:2 Energy of the nano ZnS capped with PEG polymer

No of ZnS units	E-ZnS	Band gap	E-polymer	E-merged	Adsorp-tion energy	HOMO-merged	LUMO-merged	Band gap
12	-2113.8712	4.5556	-2815.7686	-4946.684	17.0442	-9.0325	-4.4366	4.5959
18	-3407.0364	4.864	-2815.7686	-6265.1985	42.3935	-9.9909	-4.4226	5.5683
24	-4627.9304	4.4336	-2815.7686	-7444.0878	0.3888	-9.3215	-4.8924	4.4291
30	-5638.5248	4.9829	-2815.7686	-8457.804	3.5106	-9.3438	-4.4491	4.8947
36	-6730.773	3.8636	-2815.7686	-9545.9967	-0.5449	-8.997	-5.1185	3.8785

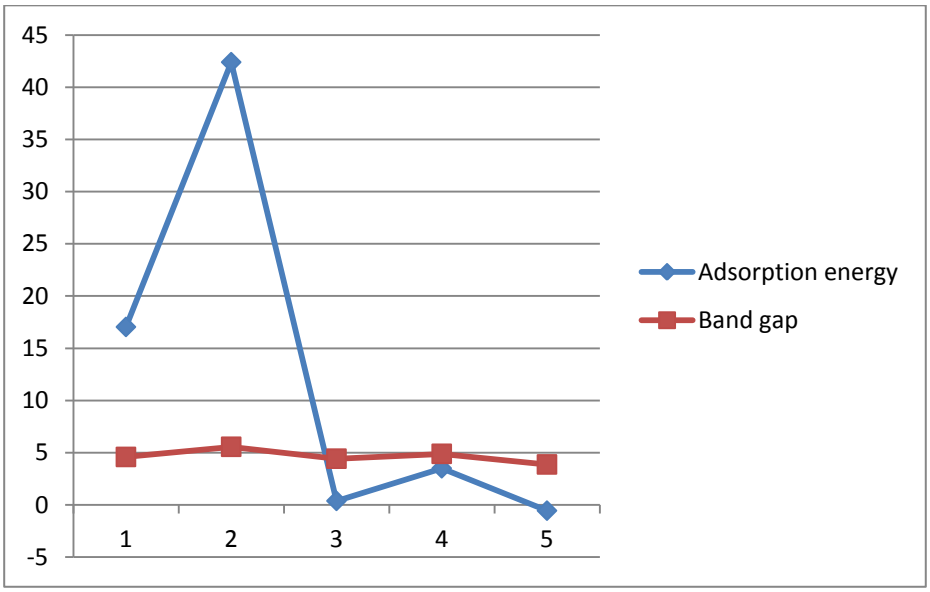

Fig:4 Trend line of ZnS adsorption energy and band gap of merged system

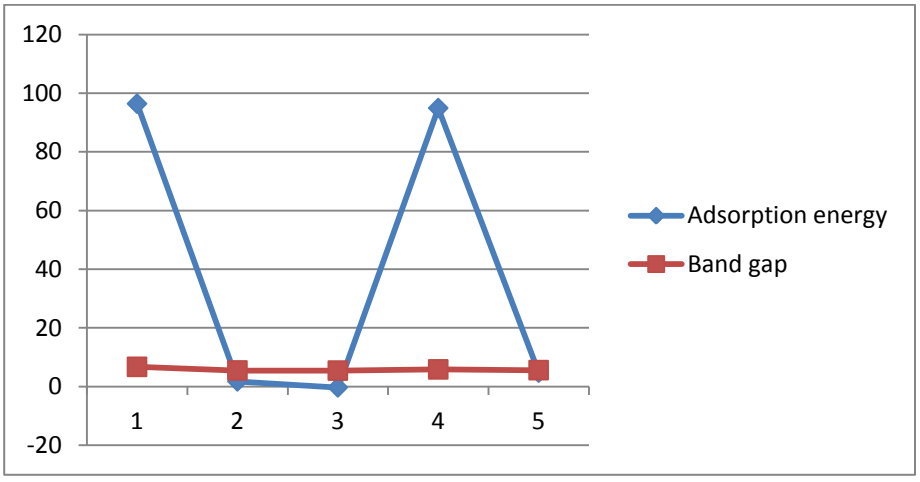

Fig:5 Trend Line of ZnO adsorption energy and band gap of merged system

is considered as an adsorption marker can be used to predict promising nano materials, which posses

desirable delivery mechanisms in biological systems. A comprehensive understanding of the unique properties of nano compounds due to their unique dimensions will go a long way in predicting the therapeutic properties as well as its preparation to the nano level in the case of nano medicines. Thus pointing towards the possibility of developing a predictive tool wherein promising nano materials may be developed based on the computational studies of band gap energy.

CONCLUSION

As an outcome of this study it was observed that there does exist a relationship that connects band energy and hydrogen bond interactions. So it can be comprehended that from computationally studying the band gap energy it will be possible to predict nano materials with desirable adsorption energy values in turn having desirable drug delivery mechanisms. This gains immense importance due to its unique properties and wide ranging applications in the field of biomedicines.

AUTHOR'S CONTRIBUTIONS

AJUC planned the project and methodology with JKR who performed the data analysis. AS, ATM and AVK supported the analysis and scientific discussions. All authors contributed to the manuscript writing. All authors have read and approved the manuscript..

ACKNOWLEDGEMENTS

The authors are grateful to the support given by the TATA-CSIR-OSDD fellowships , UGC –Centre for Cheminformatics, Malabar Christian College, Calicut.

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