Adsorption of Adipic acid in Al/B-N/P nanocages: DFT investigations

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Abstract

Drug delivery clusters based on nanocages recently have been the most capable to study. Adipic acid (ADPA) interaction mechanism over nanocages of $X(\text{Al/B})_{12}Y(\text{N/P})_{12}$ was investigated. We analyzed various electronic, chemical and spectroscopic properties with nanocages of the adsorbed ADPA molecule. Adsorption energies were calculated to study the adsorption of ADPA with nanocages. Raman enhanced surface scattering is used to track the drug as an effective approach to vibrational spectroscopy. Detection of the drug has been investigated using the SERS properties of nanocages. Title drug acts as a donor of electrons and adsorbs at the electrophilic site of nanocages. Variations in chemical descriptors to recognize the sensing property of ADPA-nanocages are also noted. Analysis of various properties explains enhancement which makes it possible to detect the drug in other products.

Introduction

In semiconductor technology, a significant challenge is to find significant terms that affect interactions of organic molecules and semiconductors [1, 2]. Studies of adsorption of molecules on semiconductors are reported [3-5]. Adipic acid (ADPA) has been used in many fields as an essential chemical raw material [6]. The use of phase-change materials in saving energy and reducing consumption is important for sustainable development in society [7-9]. ADPA is part of organic phase content with many advantages including mild super cooling and phase segregation [10]. ADPA was manufactured worldwide which mainly for nylon production. Other diverse areas used are insecticides, dying and textiles [6, 11]. A low-frequency vibrational spectrum of crystalline ADPA was reported [12]. ADPA crystal is slightly more interesting as it includes multiple close hydrogen bonds in its unit cell which are oriented differently [13]. ADPA is an important petrochemical commodity and its manufacturing process involves an emission source of greenhouse gases namely N_2O [14]. ADPA is synthesized by HNO_3 and is extremely harmful [15, 16]. ADPA, an organic acid is obtained through fatty acid hydrolysis and an important source in the chemical industry [17, 18]. Jeeva et al. reported the urea-adipic acid co-crystal synthesis and theoretical analysis [10]. Shanti et al. reported ADPA-urea content was a good centro symmetric structure having NLO properties [20]. Gopalan et al. published an analysis of a number of dicarboxylic acids with an experimental study [15]. The synthesis of polymers with isophthalic derivatives and adipic acid was reported by Kariem et al. [21]. Karlsson et al. reported ADPA tolerance screening for possible host adipic acid development [22]. With the aid of micro organisms, sustainable raw materials can be processed into ADPA [23]. Cytosine with adipic and citric acid assembly is reported by Das and Baruah [24]. Polycarboxylic acids are used in drug delivery because of their many hydrogen bond donor sites [25]. Nanostructure semiconductors have recently drawn considerable attention due to their properties [26-28]. Group III-V elements were used in microelectronics and LEDs [29-31]. AlN and BN sheets are studied as sensors and are used as adsorbents [32-34]. DFT studies of Al/B-N/P semiconductors showed that most stable are fullerenes-like $\text{X}_{12}\text{Y}_{12}$ cages [35, 36]. Due to its physical and chemical properties, $\text{Al}_{12}\text{N}_{12}$, Al_{12}P , $\text{B}_{12}\text{N}_{12}$ and $\text{B}_{12}\text{P}_{12}$ are important nanocages. Accordingly these nanocages were examined

primarily as sensors [37-44]. We are theoretically investigating the ability of four fullerene-like nanocages as adsorbents to ADPA in the present study.

Computational Methods

Calculations were carried out at wB97xD/6-31G* [45] since DFT is a powerful method for studying nanocage properties [46-48]. Adsorption energy is calculated as reported earlier [49] and charge transfer is found by the Mulliken scheme. Changes in nanocage electronic structures are evaluated by means of frontier molecular orbitals, band gap and density of states.

Results And Discussion

Electronic and Chemical properties

Initially, ADPA is placed parallel to the nanocages and allowed to relax during optimization for the most stable form (Fig.1 and Fig.2). Adsorption energies of adipic acid on AlN, AlP, BN and BP are -5.91, -5.87, -4.93 and -4.74 eV. For the adsorption of guanine on these types of nanocages, a similar trend is reported by Rad et al. [40].

The high binding energies of ADPA on aluminum nanocages suggest chemisorptions of ADPA and low energy with boron nanocages is physisorption. Adsorption of ADPA on aluminum nanocages is due to the high charge density of Al compared to B and hence aluminum nanocages are good adsorbents. ADPA's binding energy on AlN is higher than AlP nanocage which is due to charge density atoms and hydrogen bond interactions. AlN and BN nanocages are more deficient in electrons than those in AlP and BP nanocages.

Table 1 NLO properties

Drug	Dipole moment (Debye)	Polarizability ($\times 10^{-23}$ esu)	First order hyper polarizability ($\times 10^{-30}$ esu)	Second order hyper polarizability ($\times 10^{-30}$ esu)
ADPA	0.0009	1.058	0.002	-5.127
AlN-ADPA	7.7075	5.512	0.566	-42.950
AlP-ADPA	6.3004	10.050	6.333	-90.439
BN-ADPA	3.8529	3.319	0.809	-28.355
BP-ADPA	1.8617	6.894	4.008	-69.758

Charge density on AlN and BN nanocages make them susceptible to nucleophilic site. Dipole moments of free nanocages and ADPA are fundamentally zero (table 1). On adsorption of ADPA, major changes in dipole moment are observed. ADPA's dipole moment increases considerably from zero upon complexation with nanocages. Dipole moments of AlN-ADPA, AlP-ADPA, BN-ADPA and BP-ADPA are 7.71, 6.30, 3.85 and 1.86 Debye. ADPA-nanocage dipole moment variations are in line with Mulliken charge analysis. The highest shift is observed for ADPA-AlN followed by ADPA-AlP nanocage. In addition, low dipole moments for boron nanocages are due to negligible transfer of charge following adsorption with ADPA. The low charge of boron nanocages is responsible for the low dipole moments. Dipole moment vector of AlN-ADPA and AlP-ADPA originate from the cage and point away and towards ADPA while in boron nanocage the direction is from nanocage to ADPA and outward (Fig.3).

To obtain a better understanding of the mechanism of adsorption, FMOs are analyzed [50, 51]. HOMO and LUMO of ADPA (Fig.1) are located on the carboxyl group and the CH₂ near to it with a band gap of 6.70 eV showing high thermal stability of ADPA. Fermi levels of AlN, AlP, BN and BP are -4.50, -5.06, -4.29 and -4.98 eV (table 2 and Figs.S1-S4).

Table 2. Chemical descriptors

System	E_H	E_L	E_F	E_g	μD	η	μ	ω
ADPA	-9.82	-3.12	-6.47	6.70	0.0	3.35	-6.47	6.25
AIN	-6.47	-2.54	-4.50	3.93	0.0	1.97	-4.51	5.16
AIN- ADPA	-9.91	-5.27	-7.59	4.64	7.71	2.32	-7.59	12.42
AIP	-6.75	-3.36	-5.06	3.39	0.0	1.70	-5.06	7.53
AIP- ADPA	-7.48	-4.83	-6.16	2.65	6.30	1.33	-61.6	14.27
BN	-7.71	-0.86	-4.29	6.85	0.0	3.43	-4.29	2.68
BN- ADPA	-9.78	-3.47	-6.63	6.31	3.85	3.16	-6.63	6.96
BP	-6.83	-3.13	-4.98	3.70	0.0	1.85	-4.98	6.70
BP- ADPA	-7.61	-5.35	-6.48	2.26	1.86	1.13	-6.48	18.58

FMOs energy (HOMO/ LUMO) of ADPA becomes -9.91/-5.27, -7.48/-4.83, -9.78/-3.47 and -7.61/-5.35 eV and E_g values are 4.64, 2.65, 6.31, 2.26 eV after complexation. Behestian et al. [39] reported that the energy gap varies in the order BN > AIN > BP > AIP and in the present case also, the variations of energy gaps of nanoclusters ($6.85 > 3.93 > 3.7 > 3.39$) and ADPA-nanocluster systems ($6.31 > 4.64 > 2.26 > 2.65$) show the same trend. Fermi energies are -7.59, -6.16, -6.63 and -6.48 eV in AIN-ADPA, AIP-ADPA, BN-ADPA and BP-ADPA, respectively. HOMO and LUMO of nanocages are on N and P and significant changes are observed for FMOs on complexation with ADPA which is similar to the adsorption of guanine on these types of nanocages [40]. The hardness values are 2.32/1.33/3.16/1.13 for AIN/AIP/BN/BP-ADPA systems while for guanine adsorption on similar cages the corresponding values are 1.86/1.59/2.47/1.65 eV [40] which shows for these systems, the softness will increase after adsorption. In ADPA-nanocage systems, HOMO and LUMO of AIN-ADPA are situated on the COOH, CH₂ groups away from the nanocage part and on nanocage with their distributions different from free nanocages (Fig.S1). For the AIP-ADPA system, both HOMO and LUMO are over the nanocage (Fig.S2). In BN-ADPA, both FMOs are over nanocage and neighboring COOH, CH₂ groups (Fig.S3) while in BP-ADPA both are over the nanocage (Fig.S4). These changes in FMOs distribution change the band gap. Changes in band gap upon complexation are, 18.07% for AIN and 21.83% for AIP without large variation since the amounts of positive shift for FMOs are approximately the same as in DOSs (Figs.S1 and S2). Redistribution of FMOs is seen for boron nanocages and ADPA which changes the energies. The changes in band gap are 7.88% for BN and 38.90% for BP. These findings suggest that the nanocages are effective sensors for ADPA due to significant changes in the electronic properties.

To find the relation between the molecule's chemical activity MEP of ADPA with nanocages is plotted (Fig.4). Red sections are electrophilic with more electrons and blue contains nucleophilic with electron deficiency [52, 53]. For the nanocages, Al and B are positively charged (blue) whereas P and N are negatively charged (yellow) as reported by Rad et al. [40]. The charge distribution of ADPA-nanocage is investigated by the Mulliken charge values study. Carbon holds positive and negative charges and hydrogen only positive. In the case of ADPA-Al cages, carbonyl oxygen is bonded with nanocage aluminum and the charge value increases (table S1) while the oxygen atom of the OH group shows the reduction in charge while it is near to the cage. But in the case of boron-ADPA cages, the oxygen atom in the OH group is near to nanocage, whose charge decreases while the carbonyl oxygen atom's charge increases after the adsorption process. The oxygen atoms of the COOH group away from nanocages also shows the variation in charge values. The structural study of the Mulliken charge confirms chemical enhancement. UV-Vis of ADPA (150 nm) is blue-shifted in all nanocages; 591/437 nm for AlN, 476/369 AlP, 249/201 for BN and 655/600 for BP (Fig.S5).

NLO, SERS and Docking studies

Materials for nonlinear optical use are of great interest as they require technical features due to the growing usefulness of electronic instruments. NLO property of ADPA with nanoclusters is very much greater than that of ADPA which is practically zero. The second hyperpolarizability of all ADPA-nanocages shows high values in comparison with ADPA (table 1). The polarizability in contrast with that of ADPA also indicates changes in complexes [54, 55]. The high values of hyperpolarizabilities are due to the participation of excess diffuse electrons [56, 57].

SERS enhancement properties of ADPA over nanocages are noted by DFT calculations to check the drug detection. There is an enhancement for the uC-O (Fig.S6) mode of ADPA in nanocages (table S2). For AlN and AlP nanocages, only C=O stretch is enhanced while for BN and BP cages no such enhancement is seen. For all nanocages, there is an enhancement for CH₂ deformations and more modes are enhanced in AlN and AlP cages while in BN and BP this modes presence is less. In the case of nanocluster, blue shift and red shifts are observed for different modes showing interactions between ADPA and nanocages. This shows that nanoclusters will act as a sensor for the detection of drugs due to SERS [58-60].

PASS analysis [61] gives, acylcarnitine hydrolase inhibitor, alkenyl glycerophosphocholine hydrolase inhibitor, alkylacetyl glycerophosphatase inhibitor and phobic disorders treatment activities for ADPA. Corresponding PDBs, 4EP9, 1TMQ, 2HI9 and 3IDA are docked with ADPA and its complexes [62-65]. The binding energies of the nanocluster-drug complex are higher than pristine ones (table S3). For all the drug-nanoclusters, the global and atomic contact energies are greater than that of the pristine drug. Such findings give that the drugs in the study possess inhibitory effects against the receptors.

Conclusion

Adsorption of adipic acid on X12Y12 nanocages is studied theoretically. Adsorption of ADPA on Al-N/P nanocages results in high interaction energy. ADPA adsorption energies on AlN, AlP, BN, and BP cages are, -5.91, -5.87, -4.93 and -4.74 eV. At the electrophilic sites adipic acid serves as an electron donor and gets adsorbed. Charge transfer is highest for Al nanocages than for boron nanocages. Changes in the band gap, Fermi level, and other chemical descriptors are studied to understand nanocage detection capabilities. Spectral enhancement of ADPA over nanocages is observed for all nanocages. UV-vis spectra showed that the ADPA-nanocage complex is showing a trend towards higher wavenumbers. Compared to the ADPA absorption spectrum, all the nanocages-ADPA UV spectra show a blue shift in wavenumber. It is predicted that a drug delivery system will be able to use certain drugs over nanocages. Each nanocage band gap is reduced significantly at the adsorption of ADPA. Findings from the present research indicate that nanocages are suitable sensors of ADPA and ADPA is resistant to the existence of nanocages as substrate.

Declarations

Author's contributions

All authors, Jamelah S.Al-Otaibi, Y.Sheena Mary, Y.Shyma Mary, Goncagül Serdaroglu, contributed to the study conception and design, material preparation, data collections and analysis.

Conflict of interest

The authors declare that they have no conflict of interest.

Ethics approval

The manuscript is prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors

Consent to participate

The manuscript is approved by all authors for publication

Consent for publication

The consent for publication was obtained from all participants

Code availability

The calculations have been carried out using Gaussian09 and Gaussview version provided by Gaussian Inc.,

Data availability

Data is available on request to the authors

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Figures

Figure 1

The scheme of ADPA molecule along with its DOSs and HOMO-LUMO distribution

Figure 2

Optimized geometries of (a) AlN-ADPA (b) AlP-ADPA (c) BN-ADPA (d) BP-ADPA

Figure 3

The dipole moment of (a) APDA (b) AlN-ADPA (c) AlP-ADPA (d) BN-ADPA (e) BP-ADPA

Figure 4

MEP plots of (a) AlN-ADPA (b) AlP-ADPA (c) BN-ADPA (d) BP-ADPA

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