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A Comparative Computational Investigation on Amantadine Adsorption on the Surfaces of Pristine, C-, Si-, and Ga-doped Aluminum Nitride Nanosheets

Babak Mohammadi[1], Mohammad Reza Jalali Sarvestani[2,] *

[1]*Department of Chemistry, Payame Noor University, PO Box 19395-3697 Tehran, Iran*
[2]*Young Researchers and Elite Club, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran*

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ABSTRACT

Amantadine is a multipurpose medication that its determination is of great importance. Therefore, in this investigation, the performance of pristine, C-, Si-, and Ga-doped aluminum nitride nanosheets as a sensor for electrochemical detection of AT was evaluated by density functional theory computations. The calculated adsorption energies were -17.22, -19.06, -28.98, and -20.36 kcal/mol in the cases of pristine, Si-, Ga-, and C-doped nanosheets, respectively. Hence, the strongest interaction was observed between AT and Ga-doped aluminum nitride nanosheet. On the other hand, the band gap values of pristine, Si-, Ga-, and C-doped nanosheets experienced -1.81%, -10.59%, -20.74%, -2.53% decrease in the adsorption process of AT indicating when AT adsorbs on the surface of Ga-doped AlN nanosheet the electrical conductivity improved more tangibly in comparison to the other scrutinized nanostructures and this adsorbent can be used as an excellent electrocatalytic modifier for the development of novel electrochemical sensors for the detection of AT.

1. Introduction

Amantadine (AT, Figure 1) is a medication that is prescribed for the treatment of various diseases including dyskinesia, Parkinson, influenza A, Attention deficit hyperactivity disorder (ADHD), overall functional recovery in patients with brain injury, Awareness in patients with disorders of consciousness, feeling fatigue, and multiple sclerosis [1-4]. There is a narrow border between the therapeutic and toxic dosages of AT. AT is associated with serious side effects including syncope, peripheral edema, psychosis, dizziness, liver failure and Stevens–Johnson syndrome [5-8]. In this respect, rapid and accurate determination of AT is of great importance. To date various analytical methods have been reported for the determination of AT including gas-chromatography, high-performance liquid chromatography, and liquid chromatography tandem mass spectrometry [9-12]. The referred techniques although have high sensitivity and selectivity but require complicated and very expensive instruments, consume too much toxic organic solvent and are time-consuming. On the other hand, electrochemical sensors provide several privileges such as simplicity, being economic, rapidness, applicability in opaque and colored samples, the opportunity for being designed in portable forms [13-15]. However, the first step in the development of a new electrochemical sensor is finding an appropriate electrocatalytic modifier that has an adequate interaction with the desired analyte. On the other hand, aluminum nitride nanosheets (Figure 1) have special traits that make them an ideal candidate as a surface electrode modifier including high surface/volume ratio, superior electrical and structural properties and high stability [16-21]. In this respect, the interaction of AT and AlN nanosheet was investigated for the first time, in this study.

2. Results and Discussion

The AlN, Si-AlN, C-AlN, and Ga-AlN abbreviations were considered for prsitine, Si-, C-, and Ga-doped AlN nanosheets, respectively. And the abbreviations: AlN-AT, Si-AlN-AT, C-AlN-AT, and Ga-AlN-AT stand for AT complexes with prsitine, Si-, C-, and Ga-doped AlN nanosheets, respectively. As can be seen, the optimized structures of AT complexes with complexes with prsitine,

* Corresponding author.;e-mail: rezajalali93@yahoo.com
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Si-, C-, and Ga-doped AlN nanosheets are provided in Figure 2. As it is obvious, the pristine nanostructure does not have a strong interaction with AT because the optimized strucrure of the complex did not experienced sharp deformations. But, in the cases of Si-, C-, and Ga-doped AlN nanosheets the optimized structures of the created complexes showed more tangible structural changes which can be owing to the formation of chemical bonds between adsorbents and the adsorbate (AT) [9-11].

The values of total electronic energy, adsorption energy, and the bond lenghts among AT and the studied nanosheets are presented in Table 1. As the provided data in the Table show clearly the calculated adsorption energies are -17.22, -19.06, -28.98, and -20.36 kcal/mol in the cases of pristine, Si-, Ga-, and C-doped nanosheets, respectively. Hence, it can be concluded that the interaction of AT with all of the scrutinized nanostructures are experimentally possible [12-14]. AT interaction with the pristine AlN nanosheet is relatively weak because of its relatively low adsorption energy and by doping the nanosheet with silicon, carbon and gallium the interaction become stronger gradually [15]. The next point that can be perceived from the table is that

Ga-doped nanosheet has the strongest interaction with AT because it has the most negative adsorption energy among all of the investigated complexes [16].

The frontier molecular orbital (FMO) parameters were also calculated and the achieved results are presented in Table 2. The discrepancy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is known as band gap (E_g). this parameter has an inverse relationship with the electrical conductivity [9-11]. Indeed, the compounds with lower bandgap has higher conductivity than the ones with wider bandgap values. As the provided data in Table 2 show clearly, the bandgaps of AlN, Si-AlN, Ga-AlN, and C-AlN decreased -1.81%, -10.59%, -20.74%, -2.53% during the adsorption process of AT. In fact, among all of the scrutinized nanostructures the electrical conductivity of Ga-AlN experienced the most improvement and this nanosheet is the best electrocatalytic modifier for the electrochemical detection of AT. Hence, because of the strongest interaction of Ga-AlN with AT and also the remarkable reduction of bandgap during the adsorption process. It seems this nanostructure is the most appropriate surface electrode modifier for the development of novel electrochemical sensor to the determination of AT [12-15].

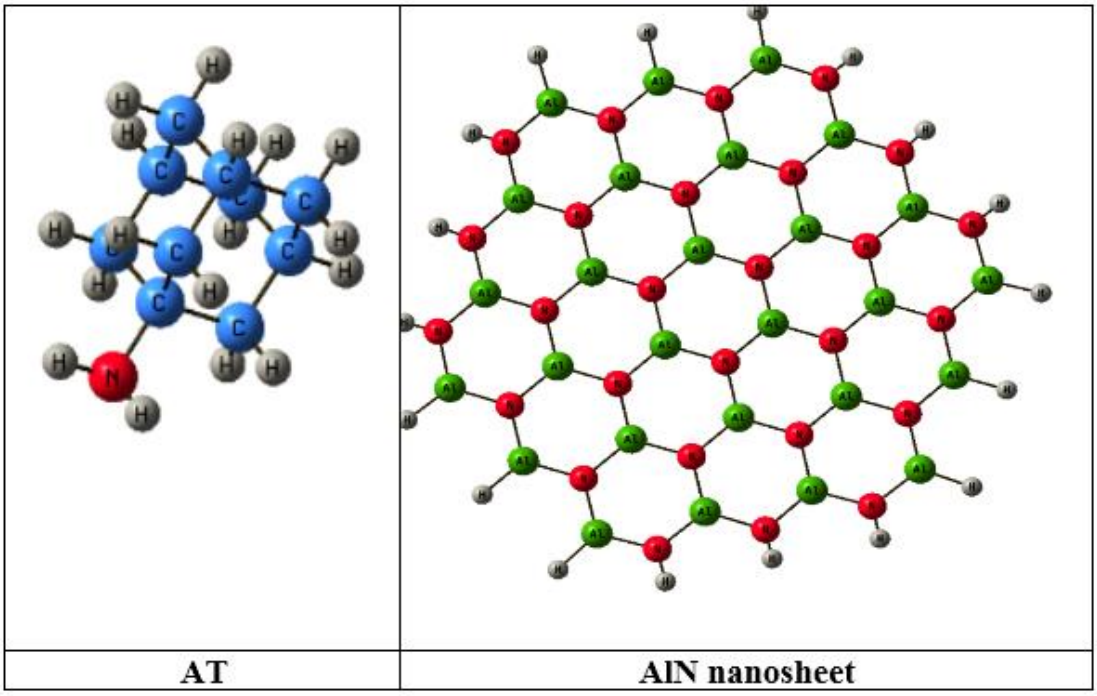

Figure 1. Optimized structures of AT and AlN nanosheet

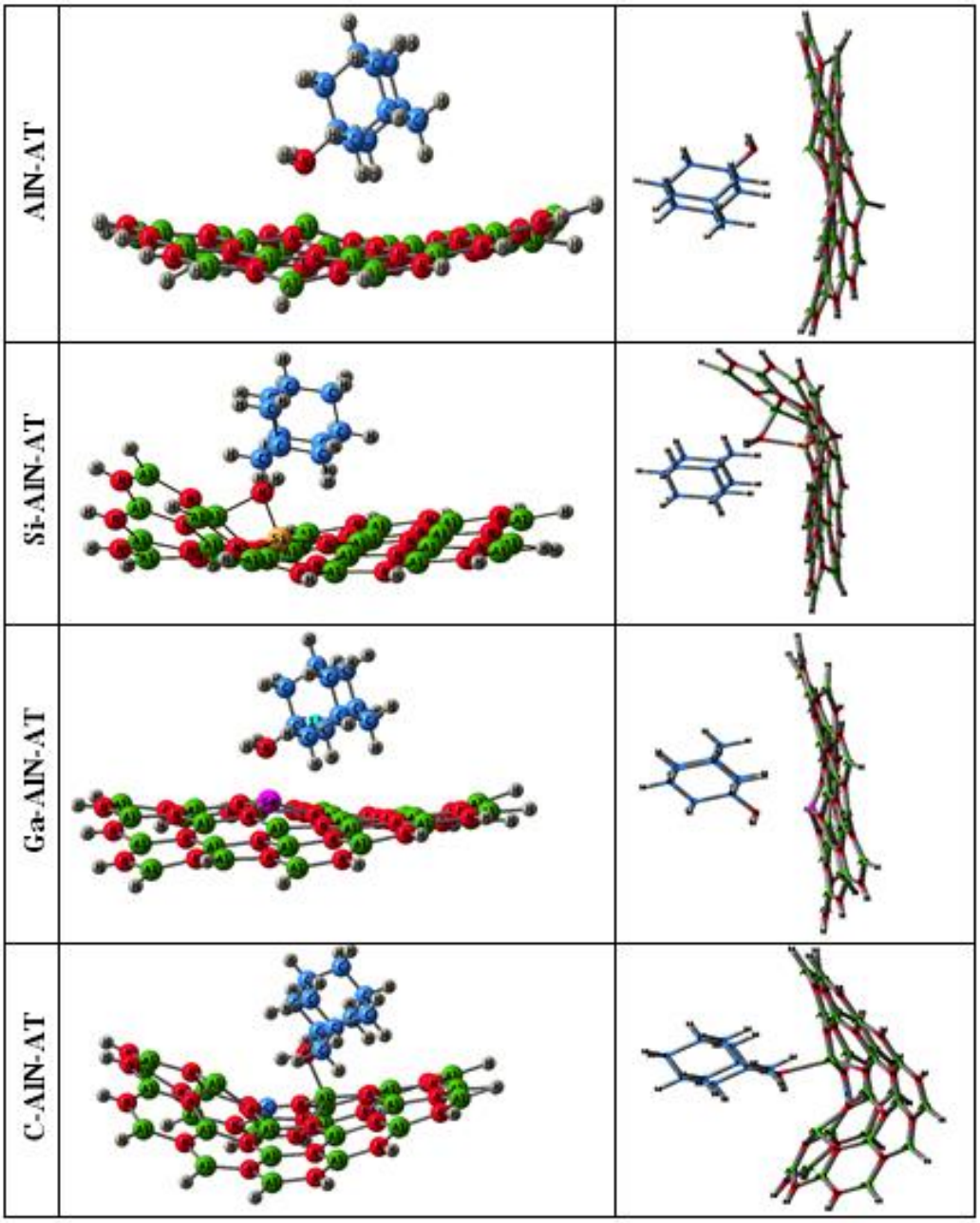

Figure 2. Optimized structures of AT complexes with prsitine, Si-, C-, and Ga-doped AlN nanosheets

Table 1. Structural propertis of AT and its complexes with prsitine, Si-, C-, and Ga-doped AlN nanosheets

	Energy (a.u)	**Energy (kcal/mol)**	**E_{ads} (kcal/mol)**	**C-N Bond length (Å)**	**Al-N Bond length (Å)**
AT	-446.0722	-279910.35	----	----	----
AlN-AT	-8483.7784	-5323570.96	-17.22	1.53	1.84
Si-AlN-AT	-8530.7622	-5353053.28	-19.06	2.06	3.41
Ga-AlN-AT	-10164.2508	-6378067.437	-28.98	1.90	1.51
C-AlN-AT	-8279.2530	-5195231.266	-20.36	1.53	2.02

Table 2. Frontier molecular orbital parameters of AT and its complexes with prsitine, Si-, C-, and Ga-doped AlN nanosheets

	E_{HOMO}(eV)	E_{LUMO}(eV)	E_g(eV)	$\%\Delta E_g$
AlN	-6.40	-1.45	4.95	-
Si-AlN	-6.45	-1.26	5.19	-
Ga-AlN	-10.79	-5.97	4.82	-
C-AlN	-6.43	-1.30	5.13	-
AT	-5.67	-1.88	3.79	-
AlN-AT	-6.12	-1.26	4.86	-1.81
Si-AlN-AT	-6.٥0	-1.40	4.64	-10.59
Ga-AlN-AT	-6.11	-1.29	4.81	-20.74
C-AlN-AT	-6.09	-1.08	5.00	-2.53

3. Computational Details

Software versions GuassView 6 [18] and Nanotube modeler 1.3.0.3 [19]were used to design the structures of pristine and doped AlN nanosheet, AT, and their complexes [20]. Each of the structures that were designed first underwent geometric optimization. After that, IR and FMO calculations were performed on designed structures. The density functional theory method was used throughout the computations by Gaussian 16 [20]software at the B3LYP/6-31G (d) level of theory[21]. This level was selected since the findings obtained from earlier studies were acceptable and were consistent with experimental results. All computations were performed in vacuum.

The following processes were investigated [9]:

AT + Adsorbent→AT-Adsorbent (1)

Adsorption energy values (E_{ad}) and the bandgap (E_g), were calculated using equations 2-4.

$$E_{ad} = \left(E_{(\text{AT-Adsorbent})} - \left(E_{(\text{AT})} + E_{(Adsorbent)} + E_{(BSSE)}\right)\right) \quad (2)$$

$$E_g = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\%\Delta E_g = \frac{E_{g2} - E_{g1}}{Eg1} \times 100 \quad (4)$$

In the equations above, E stands for the total electronic energy for every structure, E_{BSSE} stands for the basis set superposition correction, E_{LUMO}, is the energy of the lowest unoccupied molecular orbital, and E_{HOMO} is the energy of the highest occupied molecular orbital. The bandgaps of the Nano-adsorbent and AT-Adsorbent complexes are shown as E_{g1} and E_{g2}, respectively [9-13].

4. Conclusion

In this research, the applicability of four pristine, C-, Si-, and Ga-doped aluminum nitride nanosheets as an electrocatalytic sensing material for the electrochemical detection of AT was studied by DFT calculations. The obtained results showed AT interaction with all of the studied adsorbents are experimentally feasible but Ga-doped AlN nanosheet had the strongest interaction with the AT. The band gap of this nanostructure also experienced most tangible reduction in comparison to other studied nanoadsorbents. In this respect, Ga-doped AlN nanosheet can be a potential sensing material for the fabrication of new electrochemical sensors for the determination of AT.

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