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Benzoylethanamine drug interaction with the AlN nanosheet, nanotube and nanocage: Density functional theory studies

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ABSTRACT

We investigated the interaction of benzoylethanamine (BEA) drug with the AlN nanostructures including nanotube, nanocage, and nanosheet using density functional theory calculations. We predicted that the BEA molecule tends to be mainly adsorbed from its N-head on the Al atom of the AlN nanostructures with adsorption energy of −66.0, −126.2, and −147.1 kJ/mol for nanosheet, nanotube, and nanocage, respectively. This indicates that by increasing the structural curvature, the interaction is strengthened. Also, it seems that by decreasing the structural curvature of the AlN nanostructures from nanocage to the nanosheet, the kinetic stability is increased which leads to an increase in the gap. When a BEA molecule is adsorbed on the AlN nanostructures, their electrical conductivity is increased, demonstrating that they can yield an electronic signal at the presence of this molecule and can be employed in chemical sensors. The order of magnitude of the sensitivity is as follows: $S_{Nanosheet} > S_{Nanotube} > S_{Nanocage}$. We concluded that among the AlN nanostructures, the AlN nanosheet may be promising candidate for detection of BEA drug which benefits from a short recovery time of 0.33 s.

1. Introduction

Benzoylethanamine (BEA, also known as cathinone, or β-keto-amphetamine) is an organic stimulant, classified as psychoactive drug which is both similar in structure and pharmacological effect as the phenethylamine class of psychoactives (e.g. amphetamine and methamphetamine) [1,2]. Despite being controlled by drug legislation internationally BEA and its derivatives are still prevalent in numerous psychoactive substance products marketed as 'legal highs' and are sold at head shops and on the internet [3]. Abuse of these drugs has been linked to several deaths worldwide [4]. Thus, development of rapid, fast response, selective, portable, and economical sensors for their detection is still timely. Several chromatographic techniques including Gas chromatography-mass spectrometry and high performance liquid chromatography have been previously applied to detect the synthetic BEAs by different groups [5–7]. In addition to these expensive and complicated methods, a new class of sensors have been presented based on the nanostructures due to their high surface/volume ratio which is larger than that of the conventional micro detectors [8–16]. Fullerenes, graphene, and nanotubes are common nanostructures which have been widely considered as chemical sensors [17–25].

An important class of nanomaterials are based on the aluminum nitride (AlN) units including nanotubes, nanosheets, nanocages, nanocones, nanochains, etc. [26–35]. The AlN is a large band gap compound, exhibiting high stability, high hardness, high thermal conductivity, and low coefficient of thermal expansion, and it is frequently applied in thin film devices as a substrate [26–30]. These features make the AlN nanomaterials promising candidate for application in different conditions and industries. During the last decade numerous efforts have been dedicated to synthesis, characterization, and potential applications of AlN nanotubes, nanobelts, nanosheets, nanocages, nanowires, nanocones, etc. [31–37].

The most promising applications include hydrogen storage, chemical sensors, and field emitters [34–37]. The AlN nanotubes have been widely studied as chemical sensor based on the density functional theory (DFT) calculations. It has been exposed that pristine AlN nanotubes may be a potential sensor for formaldehyde which cannot be sensed by pristine carbon nanotubes [36]. Adsorption of NH_3 and NO_2 molecules on the AlN nanosheet has been investigated by Rastegar et al., indicating that NO_2 molecules can be selectively detected in the presence of NH_3 molecules [37]. Using DTF calculations, Peyghan et al. have indicated that AlN nanocage can be used to detect NO molecules in the presence of CO molecules [38]. In continuation of our works here, we explore

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the potential application of three types of AlN nanostructures including nanotube, nanosheet, and nanocage in detection of BEA drug using DFT calculations.

2. Computational methods

All calculations have been performed using the B3LYP functional with an empirical dispersion term (B3LYP-D) with 6-31G* basis set as executed in the GAMESS program [39]. The B3LYP is the commonest density functional in the investigation of nanostructured based material, reproducing experimental data [40–45]. The AlN nanostructures are a zigzag (5, 0) nanotube, an AlN nanosheet with 36 Al and 36 N atoms, and an $Al_{12}N_{12}$ nanocage. Dangling bonds of the AlN nanotube and nanosheet are saturated with hydrogen atoms to reduce the edge effects. GaussSum code was applied to draw density of states (DOS) plots [46]. The adsorption energy (E_{ad}) is calculated as follows:

$$E_{ad} = E\,(AlN) + E\,(BEA) - E\,(BEA/AlN) + E\,(BSSE) \quad (1)$$

where E (AlN) is the total energy of an AlN nanostructure. E (BEA/AlN) is the total energy of the adsorbed BEA drug on the AlN surface. E (BSSE) is the basis set superposition error (BSSE), calculate using the counter poise method [47].

The main purpose of this work is predicting the sensitivity HOMO (the highest occupied molecular orbital)-LUMO (the lowest unoccupied molecular orbital) gap (E_g) of the AlN nanostructures to the presence of BEA drug. It has been frequently demonstrated that the E_g is related to the conduction electron population (N) based on the Eq. (2) and can be applied as an appropriate index for an adsorbent sensitivity toward a chemical [48].

$$N = AT^{3/2}\exp(-E_g/2kT) \quad (2)$$

where k is the Boltzmann's constant and A (electrons/$m^3K^{3/2}$) is a constant. Some papers have revealed that there is a good agreement between the results of this technique and the experiment results [48–50].

3. Results and discussion

3.1. Optimized AlN-based nanostructured systems.

The optimized structures of the AlN nanostructures are displayed in Fig. 1. The $Al_{12}N_{12}$ nanocage is consisted from 8 hexagonal and 6 tetragonal rings with 36 Al—N bonds. These bonds can be classified in two categories including [4, 6]- and [6, 6]-bonds with average length of 1.855, and 1.793 Å, respectively. The [4, 6]-bonds are shared by a tetragon and a hexagon and [6, 6]-bonds between two hexagons. The [4, 6]-bonds are longer because of the higher strain in the tetragonal rings compared to the hexagonal ones. The molecular electrostatic potential (MEP) surface in Fig. 2 indicates that the positive and negative electrostatic potentials are mainly located on the N and Al atoms, respectively, which is in worthy agreement with the electron rich and deficient properties of N and Al atoms, respectively. The results in Table 1 show that the energies of HOMO and LUMO levels of AlN cage are −6.47 and −2.53 eV, respectively; therefore, the E_g is 3.59 eV.

Fig. 1 displays that AlN nanosheet is constructed from 33 Al, 33 N, and 22 H atoms. The equilibrium Al—N bond length of AlN nanosheet is in the range of 1.801–1.815 Å. The energy of HOMO of the sheet is −6.24 eV and that of the LUMO is −1.50 eV. So, the E_g is 4.75 eV. The AlN nanotube (Fig. 1) is a (5,0) zigzag tube with the length and dimeter of 16.514 and 5.242 Å, respectively. Two kinds of the Al—N bonds can be recognized along the tube which one is parallel with the tube axis with length of 1.815 Å and another is diagonal with length of 1.823 Å. The energies of HOMO and LUMO levels of AlN nanotube are −6.30 and −2.19 eV, respectively. The energy of HOMO level of AlN nanotube is higher and that of the LUMO is lower than the corresponding values

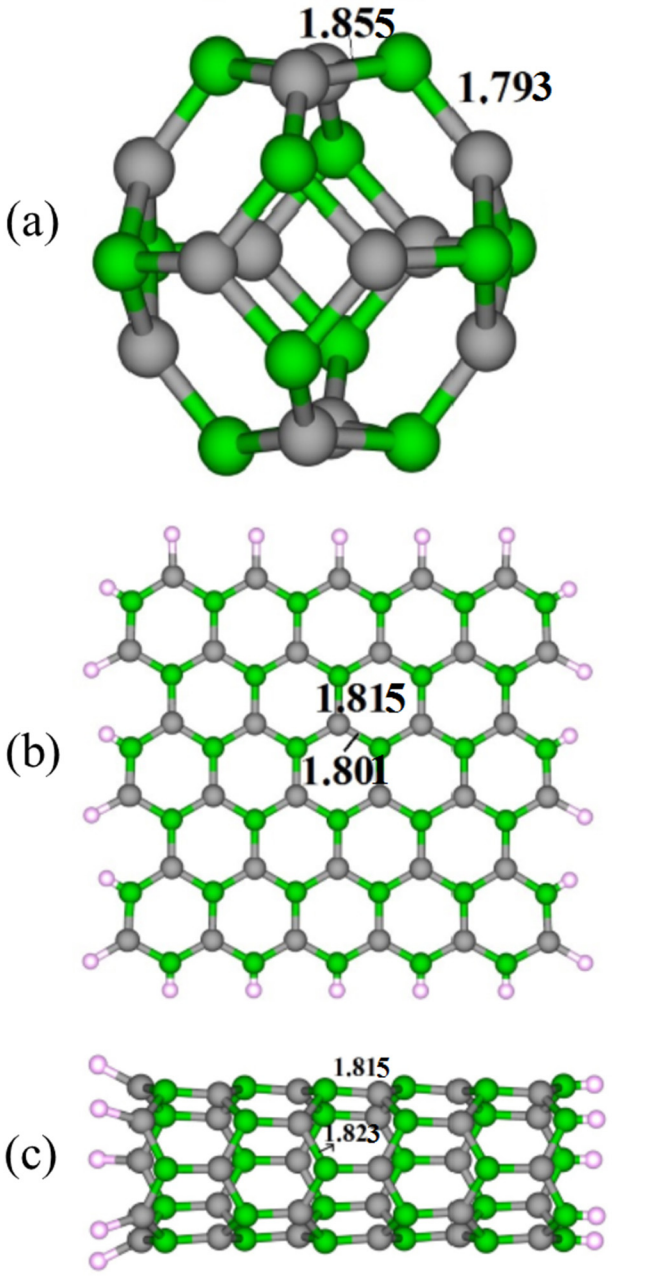

Fig. 1. The optimized structures of AlN (a) nanocage, (b) nanosheet and (c) nanotube. Distances are in Å. Green, white and gray colors indicate N, H and Al atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of AlN nanocage and, therefore, the E_g of the AlN nanotube is significantly smaller than that of the AlN nanocage. In overall, the relative order of magnitude of the E_g of the AlN nanostructures is as follows: AlN nanosheet > AlN nanotube > AlN nanocage. It has been indicated that the E_g can be related to the kinetic stability of the nanostructure and larger E_g indicates higher kinetic stability [51].

3.2. The BEA adsorption on the AlN nanocage

As it is shown in Fig. 3, the *BEA* has two nucleophile sites including carbonyl (O-head) and amine (N-head) groups which can attack to the electrophile sites (Al atoms) of the AlN nanostructures. Therefore, the optimized structures of two BEA/AlN nanocage complexes are shown in Fig. 4 in which the drug is adsorbed from its O- or N-head