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Research paper

Permeability and storage ability of inorganic $X_{12}Y_{12}$ fullerenes for lithium atom and ion

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ABSTRACT

In the current study, permeability and storage ability (exohedral and endohedral) of inorganic fullerenes $X_{12}Y_{12}$ (X = B, Al and Y = N, P) for lithium atom/ion (Li/Li^+) is studied theoretically at M05-2X method. The translation of Li/Li^+ through $Al_{12}P_{12}$ nano-cages is not only a kinetically feasible process but also has very high separation ratio in the favor of lithium atom over lithium ion. Adsorption/encapsulation energies of alkali metal on/in nano-cages show strong correlation with the size of the nano-cage. The percent changes in H-L gap for Li^+-$X_{12}Y_{12}$ are about 1–25%, whereas the corresponding changes for Li-$X_{12}Y_{12}$ are 30–72%.

1. Introduction

Continuous growing demand of energy for high power applications such as electric and hybrid electric vehicles drives the scientist to search for high energy density storage devices [1]. A variety of organic and inorganic materials have been explored in this regard. A few representative inorganic lithium storage materials are MoS_2 [2], titania nanotube, titanate nanotube [3], $Sn@V_2O_5$ [4], RuO, SnO and SnS [5]. Carbon based materials are also of particular interest for energy storage [6–10]. Carbon based materials are generally used as anode in lithium ion batteries. Fullerenes [11], graphenes [12–16], carbon nano-tubes [14,17,18], disordered carbon [19], diamond and disordered graphenes [20,21] are important carbon allotropes that have been extensively explored for high capacity storage of lithium.

Among fullerenes, C_{60} and C_{70} fullerenes are studied through cyclic voltammetry, and the results show that these fullerenes can be reduced in solution [22]. These fullerenes have also been doped with different alkali and alkaline earth metals [22]. The dopant can be placed either exohedrally or endohedrally; however, the former is more common due to synthetic challenges. Both of these sites are interstitial in nature from a defect chemical point of view. Exohedral is interstitial with respect to fullerene molecules, whereas endohedral is interstitial with respect to carbon atoms of a fullerene.

Recently, inorganic fullerenes like molecules have appeared in the literature which can potentially be applied for lithium storage. The inorganic fullerenes are quite diverse in terms of size and nature of atoms. The non-carbon fullerenes are either homo-nuclear or heteronuclear. Au_{32} and B_{40} are two most prominent examples of homo-nuclear inorganic fullerenes. Group III phosphide $((AlP)_n$, $(BP)_n)$ and nitrides $((AlN)_n$, $(BN)_n)$ alongwith group IV carbides $((SiC)_n$ and $(GeC)_n)$ are important members of hybrid nano-cages. The electronic properties of hybrid nano-cages vary remarkably among themselves to impart them low band gap to large band gap semiconducting properties [23–27].

Quite similar to other fullerenes, group III-V fullerenes $(XY)_n$ also exist in quite diverse range of sizes. A few important cage sizes are $X_{12}Y_{12}$, $X_{16}Y_{16}$, $X_{24}Y_{24}$ and $X_{28}Y_{28}$ which were the subject of several theoretical studies. $B_{12}N_{12}$ nanocluster is shown as the most stable among $B_{12}N_{12}$, $B_{16}N_{16}$ and $B_{28}N_{28}$ [28]. Similarly, $Al_{12}N_{12}$ is also the most stable cluster of (AlN)n series based on disproportionation energy and binding energy per AlN unit [24]. Beheshtian et al [29] studied the stability, geometry and electronic structure of $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ using DFT calculations. The nano-cages were also the subject of several theoretical studies aiming at exploring electronic [30], sensor [31–37], storage [38,39] and non-linear optical properties [40–44].

Quite similar to fullerene chemistry, the nano-clusters were also subjected to doping with alkali metal or transition metal atom. Doping of nano-cages is relatively well explored for NLO properties [42,43], whereas doping with transition metal is studied for sensor and hydrogen storage capacity [36]. An alkali metal or transition metal can be doped in three different ways: (a) exohedral (b)

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endohedral (c) substitutional. Exohedral doping finds further diversity due to multiple adsorption sites: (a) in the center of six membered ring (r_6), (b) in the center of four membered ring (r_4), (c) on a bond shared between two six membered rings (b_{66}), (d) on a bond shared between a four and a six membered ring (b_{64}), (e) on X atom, (f) on Y atom. Endohedral doping, on the other hand, does not find much diversity [36].

Although several reports exist on the properties of exohedral and endohedral doped nano-cages; however, detailed comparative study on ability of $X_{12}Y_{12}$ nano-cages to store lithium atom/ion is scarce. Moreover, there remains a very basic question unanswered. Can the exohedral doped atom translate inside the nano-cage through the boundary of the nano-cage? Information in this regard is really important because the barrier for this process dictates the endohedral storage of lithium. Formation of endohedral metallo fullerenes (EMF) had been a challenge since their first discovery. Laser vaporization of graphite sheet intercalated with different guest species and high energy bimolecular collision are two important approaches in this regard [45,46]. Molecular surgery method has also been applied to encapsulate guest molecules in fullerenes [47–48].

Another approach which has not been explored to any appreciable extent is rattling of an atom inside the nano-cage through the boundary of the nano-cage. This approach is quite simple however; it is not applicable to many atoms/groups due to size constraints. The only study in the literature in this regard is the translation of hydrogen through hexagon and pentagon of C_{60} fullerene [49]. The inorganic nano-cages provide additional diversity due to variation in size of hexagon. Therefore, it would be interesting to study permeability of the nano-cages for lithium atom/ion. Towards this end, lithium is chosen because of its smaller size. Moreover, the intention of study is also to explore how oxidizing lithium atom to lithium ion influences the permeability through the nano-cage. In the present study, structure, electronic properties and permeability of $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ are studied through density functional theory methods. Phosphorus nano-cages are of particular interest because of relatively large pore size compared to nitrogen nano-cages. This approach can be useful to generate EMF provided that the barriers for boundary crossing are low and the EMFs are thermodynamically quite stable. Moreover, higher barriers for exclusion of alkali metal through the nano-cage are highly desirable. The present study is detailed enough to give comparative analysis of alkali metal doping on different $X_{12}Y_{12}$ nano-cages.

2. Results and discussion

2.1. Energetic analysis

2.1.1. Adsorption energies

The geometries of Li/Li^+ doped nanocages are optimized at M05-2X/6-31G(d,p) (see Supporting Information for Computational Methodology). The numbering scheme for discussion in this study is given in Fig. 1. The optimized geometries of the Li/Li^+ doped nanocages are shown in Fig. 2 whereas the detailed geometric parameters are shown in Table S1–S4. A number of different energetic parameters are considered in this study to explore the stability of lithium doped nano-cages. Adsorption/binding energies of exohedral and endohedral complexes are calculated, and given in Table 1. A quick glance of the data reveals that binding of Li/Li^+ with all nano-cages is exothermic except encapsulation in BN nano-cage. Encapsulation of lithium atom and lithium ion in BN nano-cage is endothermic by 48.97 and 32.21 kcal mol^{-1}. Moreover, encapsulation of lithium atom in AlN nano-cage is also slightly endothermic (+1.2 kcal mol^{-1}). Despite the fact that lithium atom encapsulation in AlN nano-cage is slightly endothermic, encapsulation of lithium ion in AlN is exothermic by 22.90 kcal mol^{-1} which suggest that this complex is quite stable. Exohedral decoration of lithium atom and ion in AlN is reasonably exothermic. The binding energies of exo-Li@AlN and exo-Li^+@AlN are −42.83 and −19.93 kcal mol^{-1}. Similarly, exo-Li^+@BN nano-cage is stable by 28.06 kcal mol^{-1} compared to its components. For AlN and BN nano-cages, the endo-Li and exo-Li^+ nano-cages are the least and most stable doped nano-cages, respectively.

Endohedral doping of nitride nano-cages require high thermodynamic cost compared to corresponding phosphide nano-cages. The endothermic encapsulation can be attributed to small size of the nitride nano-cages which would lead to strong steric interactions. Phosphide nano-cages have large diameter compared to nitride nano-cages (vide infra), and can easily encapsulate lithium.

Exo-Li^+@BP is also the most stable species in BP nano-cages, whereas as the endo-Li@BP is the least stable species, a trend consistent with AlN and BN nano-cages. Doping of Li/Li^+ in BP nano-cages show some similarities with AlN and BN nano-cages; however, some differences are also observed. A clear difference in this regard is the relative stability of endohedral and exohedral complexes of a particular type. The difference in binding energies between exohedral and endohedral complexes of BP is very small when compared with AlN or BN nano-cages. The exo-Li^+@BP is just

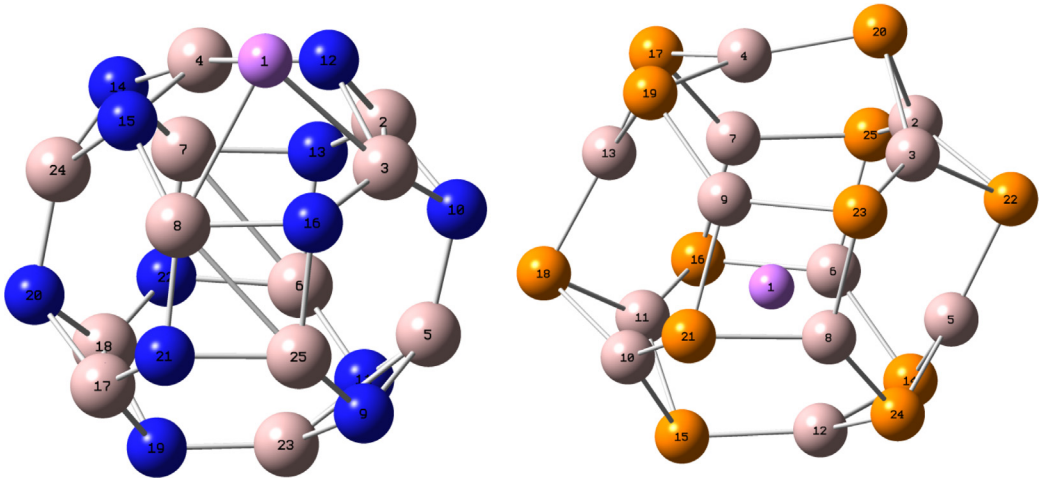

Fig. 1. Numbering scheme for lithium doped AlN and AlP nano-cages for discussion of geometric parameters.