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Hydrogen Storage on Calcium-Coated Toroidal Carbon Nanostructure C_{120} modeled with Density Functional Theory

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Ab initio density functional calculations are performed for a toroidal carbon C_{120} nanostructure doped with one to ten calcium atoms bonded to its outer surface. The calculations are based on DFT with the generalized gradient approximation PW91 (Perdew and Wang) as implemented in the Materials Studio v.4.3 code. Dmol^3 module is used to calculate, among others, total energies, charge density, HOMO-LUMO and Mulliken population analysis. Based on these results, it is possible to propose that a single Ca atom is able to adsorb up to 6 H_2 molecules. The study is extended for a system with ten Ca atoms, which can adsorb up to 60 H_2 molecules. This leads to 6.16 weight percentage for the gravimetric hydrogen storage capacity which fulfills the US Department of Energy (DOE) target (6 wt%) for onboard hydrogen storage systems for the year 2010. Accordingly, the calcium-coated toroidal carbon C_{120} nanostructure is a good quality candidate for H_2 storage with higher adsorption energy than on pristine carbon nanotorus.

Keywords: Hydrogen storage; density functional theory calculation; toroidal carbon nanostructure.

Se realizan cálculos de primeros principios con la funcional de la densidad para una nanoestructura toroidal de carbono C_{120} dopada con uno y hasta diez átomos de calcio ligados a su superficie externa. Los cálculos se basan en la teoría del funcional de la densidad (DFT), con la aproximación de gradiente generalizado PW91 (de Perdew y Wang), como aparece en el código Materials Studio v.4.3. Se usa el módulo Dmol^3 para calcular, entre otras, las energías totales, densidad de carga, orbitales moleculares ocupados más alto y más bajo y análisis de población de Mulliken. Basados en estos resultados, es posible proponer que un solo átomo de carbono es capaz de adsorber hasta 6 moléculas de hidrógeno, H_2. Esto da lugar a un porcentaje en peso de 6.16 % para la capacidad gravimétrica de almacenamiento de hidrógeno, que satisface la meta establecida de 6% para sistemas móviles de almacenamiento de hidrógeno para el año 2010 establecida por el Departamento de energía (DOE) de los Estados Unidos de América. Por lo tanto, la nanoestructura toroidal de carbono C_{120}, es un candidato de buena calidad para almacenar H_2, con una energía de adsorción más alta que en el nanotoro puro de carbono.

Descriptores: Almacenamiento de hidrógeno; cálculo con teoría funcional de la densidad; nanoestructura toroidal de carbono.

PACS: 71.15.Mb; 71.15.Nc; 81.05.Tp; 81.05.Uw

1. Introduction

Development of novel nanostructured materials for efficient hydrogen storage is of current technological interest because hydrogen is expected to replace hydrocarbons as energy source in the near future. The large surface area of the torus geometry in a given molecular species is ideal for hydrogen storage applications. Carbon nanostructures with toroidal geometry are expected to have other unusual physical properties that make them attractive for a wide range of technological applications. Dunlap proposed a toroidal carbon nanostructure with six-fold rotational symmetry in 1992 by connecting six straight nanotube segments [1]. In this work we study the all-carbon five-fold symmetric C_{120} torus as a good candidate for a hydrogen storage system. Ihara and coworkers [2] built the C_{120} nanotorus from 12 not equivalent carbon atoms.

In a recent theoretical study, Guangfen Wu *et al.* [3], investigate the feasibility of bare and metal-coated boron buckyball B_{80} with M = Li, Na, K, Be, Mg, Ca, Sc, Ti, and V for hydrogen storage using density functional theory approach. They find that M = Ca or Sc are best candidates for hydrogen storage with moderate adsorption energy of H_2 and without clustering of Sc or Ca on B_{80} surface. Qiang Sun et al [4], based on gradient corrected density functional theory, show that Li decorated B doped heterofullerene ($Li_{12}C_{48}B_{12}$) has properties of a hydrogen storage material. On the other hand, Qian Wang *et al.* [5], by means of first principles calculations based on gradient corrected density functional theory and molecular dynamics simulations of Ca decorated fullerene indicate that $C_{60}Ca_{32}$ can absorb up to 62 H_2 molecules in two layers. In addition, T. Yildirim, *et al.* [6], performed a study about molecular and dissociative adsorption of multiple hydrogen molecules on transition metal decorated C_{60}, once the metals are adsorbed on C_{60}, each can bind up to four hydrogen molecules.

In this work, we perform DFT calculations on C_{120} nanotorus with Dmol^3 code [7,8] implemented in the Materials Studio program [9]. As a first step, the stability of the isolated C_{120} nanotorus and of each of the calcium-coated nanotori with nH_2 molecules (n=1-6) was investigated. Opti-

mized geometry of C_{120} yields 4.159 and 11.740 Å for the inner and outer diameters, respectively, with a nearly circular cross section with diameter 4.623 Å. We report calculations of total energies, charge density, Mulliken population analysis and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps of these systems. The closed structure and large specific surface area of the C_{120} toroidal geometry gives room to up to 10 Ca atoms, each of which can bond to up to six H_2 molecules, suggesting that they should be efficient H_2 storage systems.

2. Theoretical method

As Ihara and coworkers [2] describe, coordinates of the 120 carbon atoms of the nanotorus were obtained from a set of 12 non equivalent carbon atoms by successive five-fold rotations followed by a reflection and final rotation of $\pi/5$ radians. The structure consists of ten pentagonal, forty hexagonal and ten heptagonal rings. Five- and six-member rings follow the *isolated pentagon rule* [10,11]. The optimized geometry of C_{120} torus is described in Table I.

We use the generalized gradient approximation of DFT implemented in the Materials Studio v.4.3 code, as proposed by Perdew and Wang (PW91) [12]. The Dmol^3 module was used to calculate, among others, total energy, electronic charge density, HOMO-LUMO and Mulliken population analysis. To calculate the interaction energies of the hydrogen molecules with the C_{120} nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). For occupied orbitals, we consider two atomic orbitals in the basis set. For C and H atoms polarization, d-function and p-function are used, respectively. The employed basis set has the advantage to be equivalent to the analytical basis set 6-31G**.

3. Results, analysis and discussion

This work has been organized in two parts. The first one is the study of the capacity of C_{120} doped with a single Ca atom externally attached (CaC_{120}) to adsorb H_2 molecules. We found that the maximum number is six, based on the corresponding average adsorption energy per H_2 (Table II). Based on this result, the second part of the present work consists on the study of C_{120} doped with 10 Ca atoms, each of them associated with 6 H_2 molecules. We add one Ca atom (and its 6 H_2 molecules) at a time, and optimize the geometries of each system before adding the next Ca.

3.1. Hydrogen storage capacity of CaC_{120}

In this section, we study hydrogen adsorption capabilities of the toroidal carbon C_{120} structure with a single Ca atom externally attached. Although a metal atom can occupy different sites of toroidal carbon C_{120} nanostructure, we consider a Ca atom adsorbed between carbon atoms labeled 85 and 86, which neighbors in a pentagonal and hexagonal ring and the respective bond length is 1.486 Å. The optimized structures of $CaC_{120}-nH_2$, for n = 1-6, are shown in Fig. 1. The geometry and energy information of calcium -toroidal carbon C_{120} nanostructure are presented in Table II. The average C-C distances involving the C atoms closest to the Ca atom (C85 y C86 in Table I) are 2.649 and 2.656 Å, respectively. The average Ca-H distances are in the range of 2.623-2.721 Å. On the other hand, the average H-H bond distances of the H_2 molecules located near the Ca atom is of 0.773 Å, as the number of H_2 molecules increases from one to six. On the contrary the C85-C86 bond distance, slightly increases from 1.484 to 1.509 Å, as the number of H_2 molecules increases from one to six

The binding energy E_b of the Ca atom adsorbed on the outer surface of the bare nanotorus is defined as [13]

$$E_b = E_t(\mathrm{Ca}) + E_t(\mathrm{C_{120}}) - E_t(\mathrm{C_{120-Ca}}) \qquad (1)$$

TABLE I. Carbon atom numbering and coordinates x, y, z (Å) in C_{120} nanotorus optimized structure.

C	x	y	z
1	2.052	0.000	0.362
2	2.364	0.000	1.767
3	2.076	2.385	2.321
4	2.909	1.239	2.321
5	4.353	1.283	2.165
6	2.564	3.745	2.166
7	5.006	0.000	1.818
8	3.889	3.734	1.558
9	4.754	2.546	1.559
10	5.818	0.001	0.617
11	5.365	2.444	0.240
12	3.982	4.346	0.239
13	0.634	-1.947	0.359
14	0.730	-2.245	1.765
15	2.909	-1.238	2.321
16	2.076	-2.384	2.321
17	2.565	-3.744	2.166
18	4.354	-1.282	2.165
19	4.754	-2.545	1.559
20	3.890	-3.733	1.558
21	3.983	-4.346	0.239
22	5.366	-2.443	0.240
23	0.730	2.246	1.765
24	1.547	4.760	1.819
25	1.661	-1.204	-0.356
26	1.548	-4.760	1.819
27	1.799	-5.532	0.617
28	-1.660	-1.205	0.356
29	-1.913	-1.390	1.760

30	-0.279	-3.148	2.318
31	-1.626	-2.711	2.318
32	-2.769	-3.597	2.169
33	0.128	-4.536	2.167
34	-4.051	-2.943	1.824
35	-0.950	-5.307	1.560
36	-2.349	-4.855	1.562
37	-4.708	-3.420	0.621
38	-2.903	-5.131	0.243
39	-0.665	-5.858	0.241
40	-1.660	1.204	0.356
41	-1.913	1.389	1.760
42	-3.082	-0.708	2.318
43	-3.082	0.707	2.318
44	-4.278	1.522	2.170
45	-4.277	-1.523	2.170
46	-4.052	2.943	1.824
47	-5.343	-0.736	1.561
48	-5.344	0.735	1.561
49	-4.708	3.420	0.621
50	-5.778	1.176	0.242
51	-5.778	-1.177	0.242
52	-1.627	2.711	2.318
53	-2.770	3.597	2.169
54	-2.350	4.855	1.562
55	-2.904	5.131	0.242
56	1.915	-1.389	-1.760
57	3.083	0.708	-2.318
58	3.083	-0.707	-2.318
59	4.279	-1.522	-2.170
60	4.279	1.523	-2.170
61	4.053	-2.943	-1.824
62	5.345	0.736	-1.561
63	5.345	-0.735	-1.561
64	4.710	-3.420	-0.621
65	5.780	-1.176	-0.242
66	5.780	1.177	-0.242
67	-0.632	-1.948	-0.359
68	-0.728	-2.246	-1.765
69	1.628	-2.711	-2.318
70	0.280	-3.148	-2.318
71	-0.125	-4.536	-2.167
72	2.771	-3.597	-2.169
73	-1.545	-4.760	-1.819
74	2.351	-4.855	-1.562
75	0.952	-5.306	-1.560
76	-1.797	-5.532	-0.617
77	0.668	-5.858	-0.241
78	2.906	-5.131	-0.242
79	-2.051	0.000	-0.362
80	-2.362	0.000	-1.767
81	-2.075	-2.385	-2.321
82	-2.908	-1.239	-2.321
83	-4.352	-1.283	-2.165
84	-2.563	-3.745	-2.166
85	-5.004	-0.001	-1.818
86	-3.888	-3.734	-1.558
87	-4.752	-2.546	-1.559
88	-5.816	-0.001	-0.617
89	-5.364	-2.444	-0.240
90	-3.981	-4.346	-0.239
91	-0.632	1.947	-0.359
92	-2.908	1.238	-2.321
93	-4.352	1.282	-2.165
94	-4.753	2.545	-1.559
95	-3.981	4.346	-0.239
96	-5.364	2.443	-0.240
97	1.662	1.205	-0.356
98	0.634	1.948	0.359
99	-0.279	3.148	2.318
100	0.127	4.536	2.167
101	-0.951	5.306	1.560
102	1.798	5.532	0.617
103	-0.666	5.858	0.241
104	-0.729	2.245	-1.765
105	-2.075	2.384	-2.321
106	-2.564	3.744	-2.166
107	-1.546	4.760	-1.819
108	-3.889	3.733	-1.558
109	-1.798	5.532	-0.618
110	1.915	1.389	-1.760
111	0.280	3.148	-2.319
112	1.628	2.711	-2.318
113	2.770	3.597	-2.169
114	-0.126	4.536	-2.167
115	4.052	2.943	-1.824
116	0.951	5.307	-1.560
117	2.350	4.855	-1.562
118	4.709	3.420	-0.621
119	2.905	5.131	-0.243
120	0.666	5.858	-0.241

where E_t (Ca), E_t (C_{120}) and E_t (C_{120-Ca}) are the total energies of a free Ca atom, the pure C_{120} and the C_{120-Ca}

system, respectively. E_b is found to be equal to 4.630 (eV), which indicates that the C_{120}-Ca system is strongly bonded. The strength of the interaction is consistent with the formation of a C-Ca bond, which indicates that the whole system can be considered as one single species.

We have also computed the average adsorption energy per H_2, [3]

$$E_{\text{ave}}=\{E[\text{CaC}_{120}]+nE[\text{H}_2]-E[\text{CaC}_{120}-n\text{H}_2]\}/n \quad (2)$$

and consecutive adsorption energy of H_2

$$E_t = E[\text{CaC}_{120}-(n-1)\text{H}_2] + E[\text{H}_2]-E[\text{CaC}_{120}-n\text{H}_2] \quad (3)$$

where $E[\text{CaC}_{120}]$, $E[\text{H}_2]$, $E[\text{CaC}_{120}-n\text{H}_2]$ and $E[\text{CaC}_{120}$-$(n$-1)$\text{H}_2]$ are the total energies of relaxed CaC_{120}, H_2 molecule, $\text{CaC}_{120}-n\text{H}_2$ and the CaC_{120}-$(n$-1)H_2 system, respectively, and n is the number of H_2 molecules, see Table II. Although the adsorption energy of the first H_2 on CaC_{120} reaches up to 0.151 eV, that of the second H_2 is 0.201 eV. The stronger binding of H_2 to CaC_{120} and the relatively larger HOMO-LUMO gap of CaC_{120}-H_2 imply that this structure is of high stability. Thus, the second H_2 is very easy to adsorb. For the other H_2 molecules, the value of adsorption energy slightly decreases from 0.201 for two H_2 molecules to 0.084 eV, for six H_2 molecules. However, even for the latter there is a strong binding of H_2 to CaC_{120}. Accordingly, the system CaC_{120}-6H_2 is stable and expected to be a good alternative for hydrogen storage.

The spatial HOMO-LUMO distributions for the bare CaC_{120} and hydrogenated CaC_{120}-6H_2 system are shown correspondingly in Figs. 2 and 3, respectively. Blue lobes

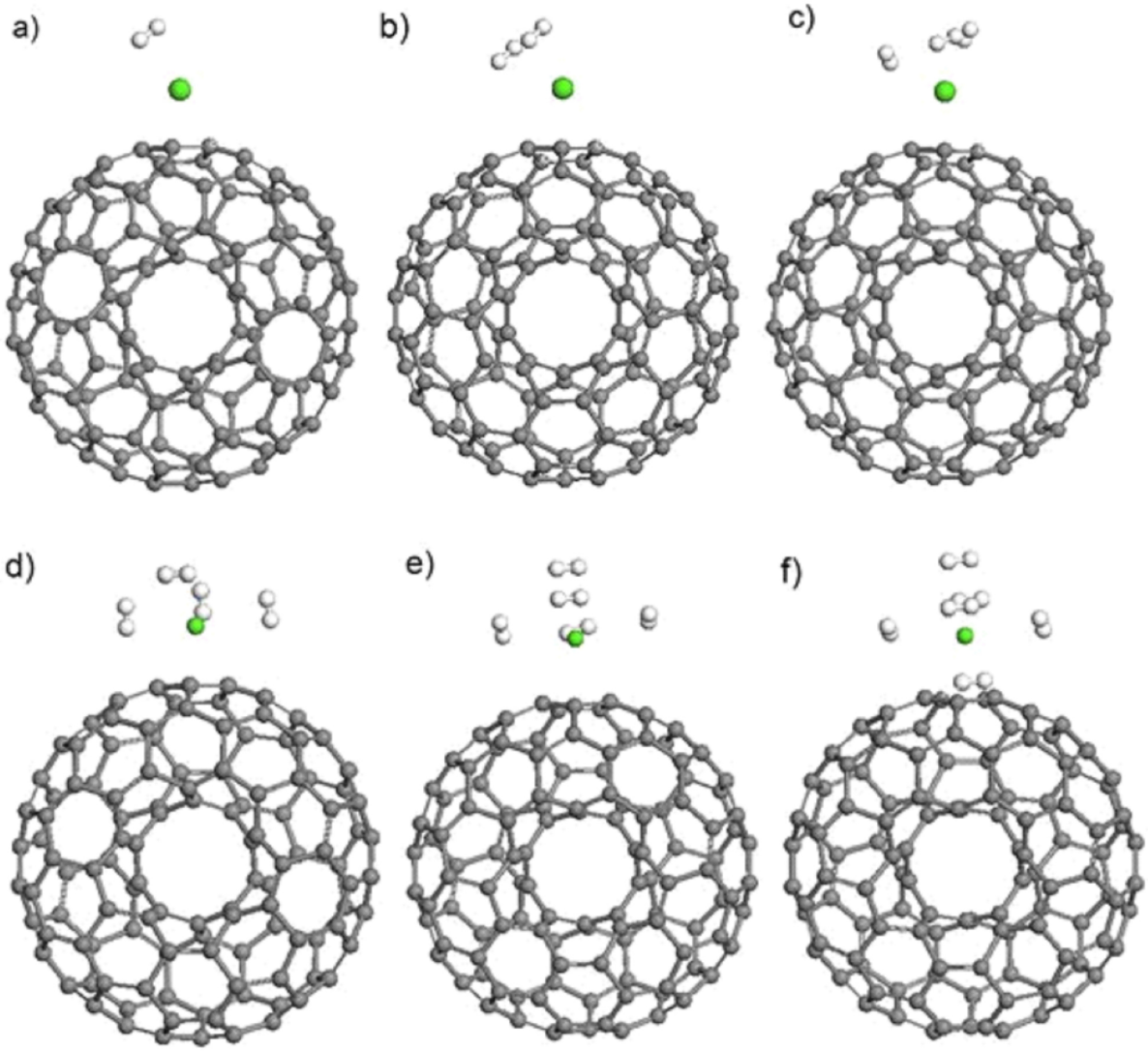

FIGURE 1. (a - f) Optimized structures of $\text{CaC}_{120}-n\text{H}_2$ systems, for n = (1-6) respectively.

TABLE II. Total energy, average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2, and geometrics parameters of CaC_{120} and $CaC_{120} - nH_2$ n = (1-6) systems.

System	Total Energy (Ha)	Average adsorption energy per H_2 (eV)	Distances (Å)				Average H-H bond lengths (Å)
			C86-Ca	C85-Ca	Average Ca-H	C85-C86	
CaC_{120}	-5251.436127	–	2.674	2.696	–	1.484	–
CaC_{120}-H_2	-5252.610773	0.151	2.611	2.631	2.721	1.493	0.772
CaC_{120}-$2H_2$	-5253.787271	0.176 (0.201)	2.676	2.686	2.623	1.485	0.774
CaC_{120}-$3H_2$	-5254.962808	0.176 (0.175)	2.709	2.662	2.633	1.487	0.774
CaC_{120}-$4H_2$	-5256.139268	0.182 (0.200)	2.643	2.638	2.631	1.488	0.773
CaC_{120}-$5H_2$	-5257.315292	0.183 (0.188)	2.657	2.634	2.659	1.487	0.772
CaC_{120}-$6H_2$	-5258.487476	0.167 (0.084)	2.624	2.595	2.643	1.509	0.772

TABLE III. HOMO-LUMO energies and gap (Δ) of CaC_{120} and $CaC_{120} - nH_2$ n = (1-6) system in eV.

System	HOMO	LUMO	(Δ)
CaC_{120}	-5.57	-4.59	0.98
CaC_{120}-H_2	-5.57	-4.59	0.98
CaC_{120}-$2H_2$	-5.58	-4.59	0.99
CaC_{120}-$3H_2$	-5.58	-4.60	0.98
CaC_{120}-$4H_2$	-5.58	-4.60	0.98
CaC_{120}-$5H_2$	-5.58	-4.60	0.98
CaC_{120}-$6H_2$	-5.57	-4.59	0.98

show the positive and yellow lobes show the negative values of the wave function.

In Fig. 2, the density distribution in the LUMO of CaC_{120} systems is mainly located in the neighborhood of the Ca atom, indicating that the adsorption of the first H_2 molecule is expected to take place in this region. The Fig. 3 shows the CaC_{120}-$6H_2$ system. The LUMO density is also concentrated in the vicinity of the Ca atom, suggesting that the second molecule of H_2 would also be absorbed in this region.

The HOMO-LUMO energy gaps (Δ) of CaC_{120} and $CaC_{120} - nH_2$ n = (1-6) system are reported in Table III. They are very similar for all the reported systems with average values of 0.98 eV.

The values for the Mulliken population analysis are on Table IV. According to them for the system with only one atom of Ca without H_2 molecules, the value is 0.993 electrons. This means there is a very high charge transfer from this atom to the C atoms that are closer and labeled with numbers 85, 86, 88 and 89. For the rest of the Ca atoms, as the number of H_2 molecules increases the value of its charge transfer lowers from 0.979 for one H_2 molecule to 1.016 electrons for 6 hydrogen molecules.

From Table IV it is also possible to observe that when 1 to 5 molecules of H_2 are adsorbed, the charge transfer to these carbon atoms is almost the same for all (-0.135 electrons in average). But when the number of hydrogen molecules increase to 6, then the charge transfer also increase towards the carbon atoms labeled with numbers 85 and 86 (-0.297 electrons in average). Regarding the hydrogen, these transfer their charge and stabilize in an average value of 0.016 electrons.

3.2. Hydrogen storage capacity of 10CaC_{120}

Now we know that a single atom of Ca can adsorb up to six molecules of H_2. In this section of our study, we cover C_{120}

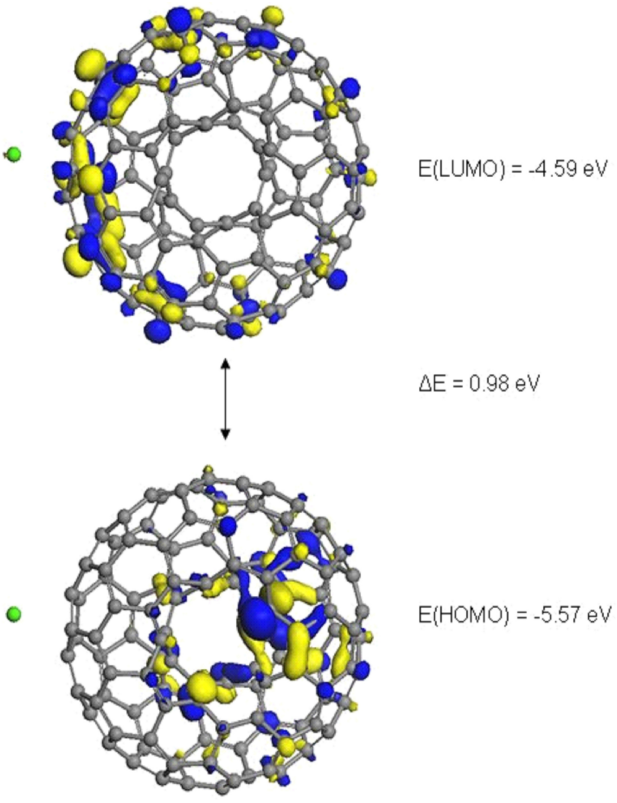

FIGURE 2. HOMO-LUMO energy gap (Δ) for the CaC_{120} system. Above: E(LUMO)=-4.59 eV. Below: E(HOMO)= -5.57 eV. ΔE = 0.98 eV.

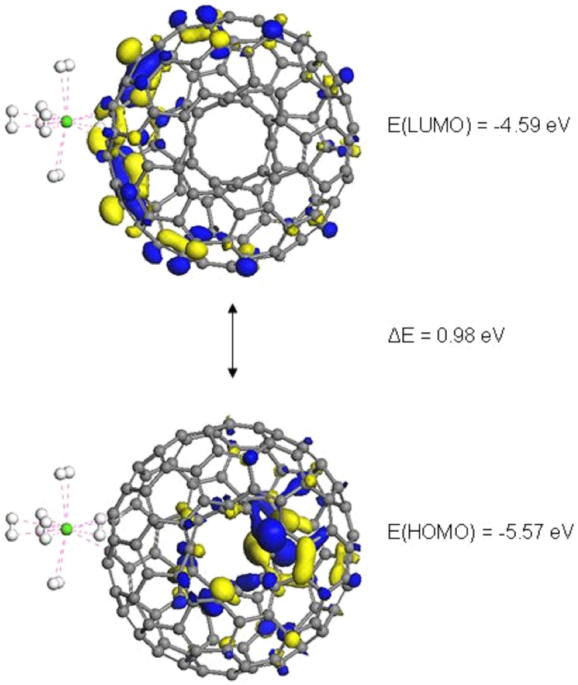

FIGURE 3. HOMO-LUMO energy gap (Δ) for the CaC_{120}-$6H_2$ system. Above: E(LUMO)= -4.59 eV. Below: E(HOMO)=-5.57 eV. ΔE = 0.98 eV.

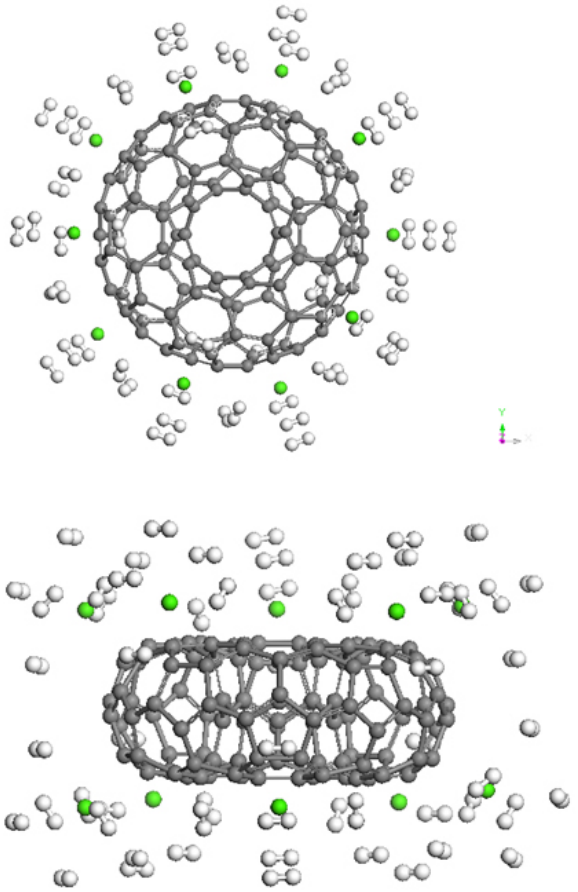

FIGURE 4. Optimized structure of $10CaC_{120}$-$60H_2$ system. Upper view (above) and side view (below).

TABLE IV. Mulliken population analysis of $CaC_{120}$and $CaC_{120} - nH_2$ n = (1-6) system.

System	Mulliken charge (electron)		
	Ca atom	H atom Average	C atom
CaC_{120}	0.933	–	C85 -0.131
			C86 -0.139
			C88 -0.171
			C89 -0.150
CaC_{120}-H_2	0.979	-0.015	C85 -0.161
			C86 -0.171
			C88 -0.148
			C89 -0.141
CaC_{120}-$2H_2$	1.016	-0.019	C85 -0.135
			C86 -0.133
			C88 -0.169
			C89 -0.160
CaC_{120}-$3H_2$	1.072	-0.021	C85 -0.137
			C86 -0.109
			C88 -0.160
			C89 -0.193
CaC_{120}-$4H_2$	1.086	-0.016	C85 -0.154
			C86 -0.151
			C88 -0.157
			C89 -0.160
CaC_{120}-$5H_2$	1.085	-0.014	C85 -0.155
			C86 -0.146
			C88 -0.147
			C89 -0.160
CaC_{120}-$6H_2$	1.016	-0.014	C85 -0.309
			C86 -0.286
			C88 0.036
			C89 0.033

with more Ca atoms and thus we find up to now and without external pressure, that the maximum number is 10 ($10CaC_{120}$), giving us 60 H_2 molecules. This represents a 6.16 percentage in weight, which complies with the U.S. Department of Energy (USDOE) goal for the year 2010 (6 wt%) for materials designed to store hydrogen.

Figure 4 shows many sites around the middle plane of the nanotorus that can be coated with more calcium atoms and hydrogen molecules. This will be explored with the application of external pressure and will be reported elsewhere. A second group of hydrogen molecules around the first one could possibly be bonded in addition but with an expected binding energy less than for the nearest hydrogen molecules to the calcium and carbon atoms.

Figure 4 shows the geometry optimized system $10CaC_{120}$-$60H_2$. The total energy values obtained for all systems from

TABLE V. Total energy, HOMO-LUMO energy gap (Δ) and geometrics parameters of CaC_{120} and $nCaC_{120}$-$(6n)H_2$ n=1-10 systems.

System	Total Energy (Ha)	(Δ) (eV)	Distances (Å)			Average H-H bond lengths (Å)
			Average C-Ca	Average Ca-H	Average C(1)-C(2)	
CaC_{120}	-5251.436127	0.98	2.688	–	1.509	–
CaC_{120}-$6H_2$	-5258.487476	0.98	2.609	2.643	1.509	0.772
$2CaC_{120}$-$12H_2$	-5943.243964	0.92	2.608	2.647	1.510	0.773
$3CaC_{120}$-$18H_2$	-6627.999257	0.88	2.596	2.683	1.512	0.773
$4CaC_{120}$-$24H_2$	-7312.753049	0.87	2.611	2.698	1.512	0.773
$5CaC_{120}$-$30H_2$	-7997.505069	0.86	2.593	2.695	1.512	0.776
$6CaC_{120}$-$36H_2$	-8682.255838	0.81	2.593	2.695	1.511	0.775
$7CaC_{120}$-$42H_2$	-9367.008956	0.11	2.591	2.679	1.509	0.775
$8CaC_{120}$-$48H_2$	-10051.756726	0.12	2.590	2.676	1.508	0.776
$9CaC_{120}$-$54H_2$	-10736.504581	0.12	2.583	2.686	1.507	0.776
$10CaC_{120}$-$60H_2$	-11421.253482	0.21	2.592	2.677	1.507	0.776

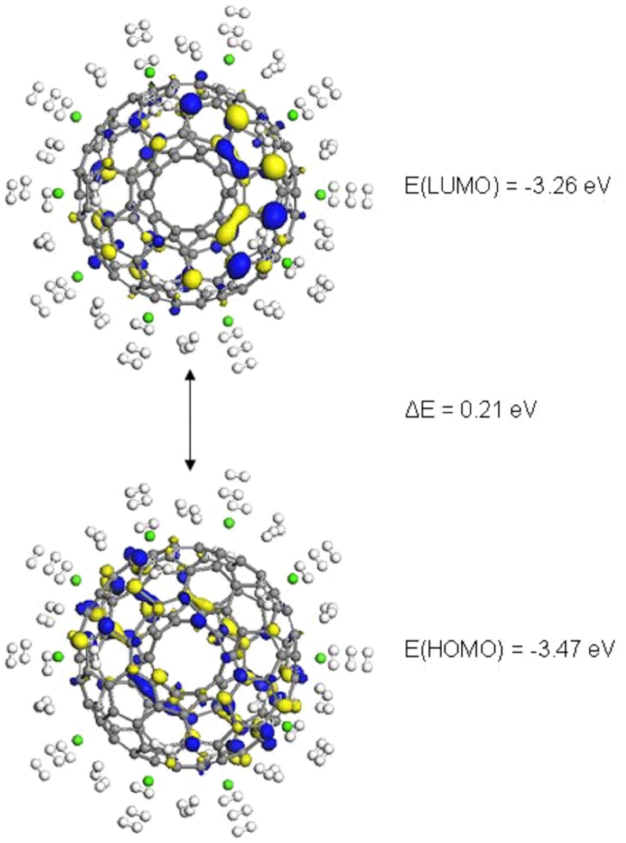

FIGURE 5. HOMO-LUMO energy gap (Δ) for the $10CaC_{120}$-$60H_2$ system. Above: E(LUMO)= -3.26 eV. Below: E(HOMO)= -3.47 eV. ΔE = 0.21 eV.

one to 10 Ca atoms is on Table V. The values HOMO-LUMO energy gaps (Δ) and geometric parameters of optimization are given.

From values in Table V, it is possible to conclude that as the number of calcium atoms increases, the gap value decreases from 0.98 to 0.21 eV, for 1 and 10 Ca atoms, respectively. Note that for seven Ca atoms there is a minimal gap value of 0.11 eV. This means that the chemical reactivity of the system increases. The distance is inside the same range; except for the average of the H-H bond, that with single Ca atom is 0.772 Å. As the number of Ca atoms increases, the bond length increases slightly up to 0.776 Å with 10 Ca atoms.

In Fig. 5 it can be seen that the HOMO and LUMO of the $10CaC_{120}$-$60H_2$ system are nearly uniformly distributed on the external surface of C_{120}.

We have computed the Mulliken populations for all the studied systems. The Mulliken charges on the Ca atom, H atom and C atom are in Table VI. We can conclude from this

TABLE VI. Mulliken population analysis of CaC_{120} and $nCaC_{120}$-$(6n)H_2$ n=1-10 systems.

System	Mulliken charge (electron)		
	Ca atom Average	H atom Average	C atom Average
CaC_{120}	0.933	–	-0.121
CaC_{120}-$6H_2$	1.016	-0.023	-0.297
$2CaC_{120}$-$12H_2$	1.014	-0.031	-0.299
$3CaC_{120}$-$18H_2$	1.017	-0.025	-0.304
$4CaC_{120}$-$24H_2$	1.015	-0.028	-0.306
$5CaC_{120}$-$30H_2$	1.013	-0.020	-0.305
$6CaC_{120}$-$36H_2$	1.010	-0.021	-0.302
$7CaC_{120}$-$42H_2$	1.010	-0.027	-0.282
$8CaC_{120}$-$48H_2$	1.011	-0.031	-0.289
$9CaC_{120}$-$54H_2$	1.010	-0.034	-0.293
$10CaC_{120}$-$60H_2$	1.009	-0.032	-0.290

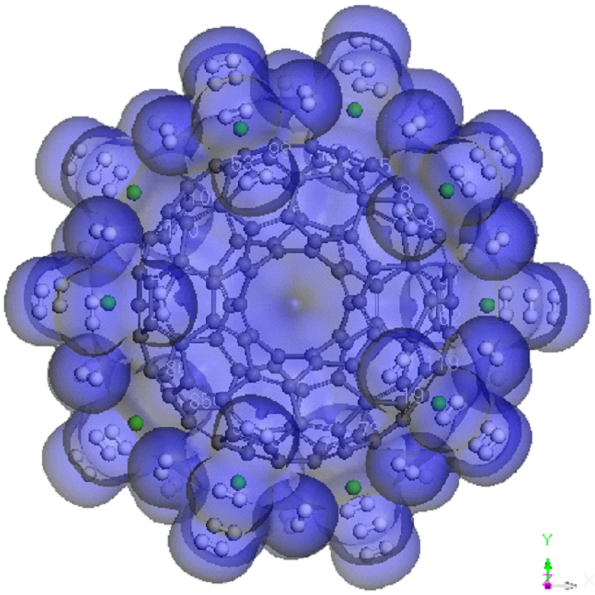

FIGURE 6. Top view of the calculated total charge density of $10CaC_{120}$-$60H_2$. The gray and dark-gray atoms are H and C, respectively. (Blue color isovalue = 0.017).

table that for the system with a single Ca atom without H_2 molecules, there is a charge transfer of 0.933 electrons from Ca atom towards the C atom of -0.121 electrons (average of C atoms neighboring the Ca atom). For the systems with several Ca atoms that have H_2 molecules, there is also a charge transfer from the Ca atoms (1.012 average electrons) towards the C atoms (- 0.297 average electrons) keeping all the values within the same range. In the case of the hydrogen atoms, it is observed that the average charge transfer is of -0.027 electrons.

Finally, the total charge density for the system with 60 H_2 molecules is in Fig. 6. The final equilibrium configuration for this case has a high symmetry distribution for all the atoms and in the charge density as well.

4. Summary

We have studied the hydrogen adsorption capabilities of toroidal carbon C_{120} structure with a single metal (Ca) externally attached, these shows to be good candidate for hydrogen storage with higher H_2 adsorption energy than for pristine carbon nanotorus. The maximum number of H_2 molecules to be absorbed near the Ca atom is six. The system with 10 Ca atoms can adsorb up to 60 molecules of H_2, which represents 6.16 wt percentage, which fulfils the current requirement (6 wt %, in 2010, specified by US Department of Energy.

5. Conclusions

Geometry optimization and several properties of all the studied systems were calculated. The binding energy is calculated as function of the number of hydrogen atoms. The results let us to conclude that hydrogen storage is possible in the Ca-C_{120} nanotorus system, reaching up to 6.16 wt %, for the system with 10 Ca atoms. Other possibilities to increase the quantity of hydrogen bounded to the system are under study. These results will be reported elsewhere.

The average H-H bond length is close to 0.774 Å for 1-$10CaC_{120}$ systems (see Table V). This length is a little bit greater than 0.7430 Å, the isolated length for the hydrogen molecule, as expected. In a recent work [14], hydrogen storage capacity is studied for a C_{120} nanocapsule. They obtain -0.03 eV and 2.384 Å for the absorption energy of one hydrogen molecule on the outer surface of the tube and for the average C-H equilibrium distance, respectively. In our case, for only one hydrogen molecule we obtain for the system $CaC_{120}H_2$ absorption energy of 0.151 eV and 0.772 Å for the average H-H bond length.

B_{80} fullerene coated with 12 Ca atoms can store 60 H_2 molecules with an average binding energy of 0.14 - 0.40 eV [15]. For a Ca covered B (9,0) nanotube, the hydrogen binding energy is 0.1-0.3 eV/H_2. A common and interesting feature of these systems with Ca atoms is that they became attractive for high hydrogen storage purposes.

Respect to other type of properties, it will be interesting to study for example, the possible semiconducting properties of cubic (fcc or sc) crystalline C_{120} nanotorus and establish some comparison with the semiconducting properties exhibited by the fullerene C_{60}.

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