

Hexagonal-Like Carbon Nanocage Enhanced Selective Sensing toward Organic Molecules

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Abstract

Selective sensing technologies have attracted considerable attention due to the broad range of their applications in environmental monitoring, industrial and public safety, as well as in chemical analysis and molecular electronics. Here, we propose a novel hexagonal-like carbon nanocage (*h*-LCNC) as a nanosensor for selective sensing toward three organic molecules, namely benzene (BZ), tetracyanoethylene (TCNE), and tetrathiafulvalene (TTF). First-principles density functional theory (DFT) was carried out to investigate the electronic structure and selective sensing performance of the *h*-LCNC. Density of states (DOS) calculations show that the bare *h*-LCNC is a semiconductor with an energy gap of 0.764 eV. The sensing performance of the *h*-LCNC was assessed through structural relaxation, DOS, local density of states (LDOS), adsorption energy (E_{ads}), charge transfer (Ch_{Tr}), and recovery time (τ) analyses. These results reveal different interactions between the molecules and the *h*-LCNC surface, which translate into distinct DOS, LDOS, E_{ads} , Ch_{Tr} , and τ responses that enable efficient discrimination among the BZ, TCNE, and TTF molecules. These findings provide a promising basis for the development of more accurate and sensitive nanoscale sensors.

Keywords: Carbon nanocage, Density functional theory, Selective sensing.

ققص نانوي كربوني شبيه بالبنية السداسية لتعزيز التحسس الانتقائي للجزئيات العضوية

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الخلاصة

حظيت تقنيات التحسس الانتقائي باهتمام كبير نظراً لتعدد تطبيقاتها في مجالات الرصد البيئي، والسلامة الصناعية والعمامة، بالإضافة إلى التحليل الكيميائي والإلكترونيات الجزيئية. في هذه الدراسة، نقترح قفصاً نانويًا كربونيًا جديدًا ذا بنية سداسية الشكل (*h*-LCNC) ليعمل كمستشعر نانوي للتحسس الانتقائي لثلاثة جزيئات عضوية، هي البنزين (BZ)، ورباعي سيانوالاينيلين (TCNE)، ورباعي ثيافولفالين (TTF). وقد استخدمت حسابات نظرية دالة الكثافة (DFT) المبنية على المبادئ الأولى لدراسة البنية الإلكترونية وأداء التحسس الانتقائي للقفص النانوي المقترح. وأظهرت حسابات كثافة الحالات الإلكترونية (DOS) أن القفص النانوي *h*-LCNC في حالته المجردة يتمتع بخواص شبه موصلة، بفجوة طاقة مقدارها 0.764 إلكترون فولت. وتم تقييم أداء التحسس للقفص النانوي *h*-LCNC من خلال تحليلات الاسترخاء البنيوي، وكثافة الحالات الإلكترونية (DOS)، وكثافة الحالات الإلكترونية الموضعية (LDOS)، وطاقة الامتزاز (E_{ads})، وانتقال الشحنة (Ch_{Tr})، وزمن الاستعادة (τ). وأظهرت النتائج وجود تفاعلات مختلفة بين الجزيئات وسطح القفص النانوي *h*-LCNC، انعكست في استجابات مميزة لكل من DOS و LDOS و E_{ads} و Ch_{Tr} و τ ، مما أتاح التمييز بكفاءة بين جزيئات البنزين (BZ)، ورباعي سيانوالاينيلين (TCNE)، ورباعي ثيافولفالين (TTF). وتوفر هذه النتائج أساساً واعدًا لتطوير مستشعرات نانوية أكثر دقة وحساسية.

1. Introduction

Development of rapid-responding, reliable, on-site, and low-cost nanosensors has attracted considerable interest from many research groups and scientists [1-3], due to their

widespread applications, including environmental monitoring [4-6], industrial safety [7-9], national security [10-12]. Discriminative sensing plays an essential role in chemical analysis in which identification of chemically similar molecules is fundamental for reliable quantitative and qualitative measurements [13, 14]. Similarly, in molecular electronics, adsorption-induced alterations in the electronic properties of nanostructured materials provide distinct electronic fingerprints that allow for selective identification of targeted analytes [15, 16]. Recently, experimental published studies [17, 18] have also revealed that the optical and electronic properties of nanoscale materials are highly sensitive to molecular adsorption and environmental conditions, providing further support for their potential in detecting applications. Traditional analytical methods [19, 20] frequently require sophisticated instrumentation, high operational costs, complicated sample preparation procedures. On the other hand, nanomaterial-based sensors [21, 22] offer rapid, portable, and label-free sensing with high sensitivity performance. Nanomaterials based on carbon represent promising candidates, including graphene, carbon nanotubes, and fullerenes, for chemical and molecular sensing applications as they can distinguish between target molecules [23-28]. Among a variety of approaches for developing new nanostructures, the sculpture method [29] is used to construct a unique family of sp^2 -bonded nanomaterials, including heterostructured nanomaterials, through spontaneous reconstruction of carved bilayer/multilayer materials. This method is a theoretical framework proposed to obtain novel nanostructural geometries by sculpting bilayer graphene or other layered materials into desired shapes and allowing them to spontaneously reconstruct their open edges to form stable sp^2 -bonded architectures. This fabrication process enables the development of unique carbon nanocages with configurations that are challenging to generate using traditional synthesis techniques, while maintaining outstanding structural stability and refining electronic properties [29, 30]. Interestingly, recent experimental studies [31, 32] have demonstrated the spontaneous reconstruction of bilayer graphene into sp^2 -bonded carbon nanostructures, which providing strong evidence for the experimental feasibility of the sculpture method. The sculpture-based carbon nanocages provide desirable platforms for investigating adsorption-induced tunability and selective sensing toward single-molecule applications due to their quantum confinement and large surface area. There have also been theoretical works reporting similar molecular selective sensing concepts according to π -conjugated nanostructures, in which donor and acceptor analytes produce unique electronic fingerprints that allow for discrimination different analytes [33]. Benzene (BZ, C_6H_6), Tetracyanoethylene (TCNE, C_6N_4), and Tetrathiafulvalene (TTF, $C_6H_4S_4$) molecules exhibit fundamentally distinct electronic properties and hence offer a useful criterion for assessing materials for selective sensing. BZ is a volatile aromatic organic compound and an environmental contaminant whose identification is highly important because of its toxicity and extensive use in industry [34, 35]. TCNE, in contrast, is a well-known organic molecule and one of the strongest electron acceptors [36], whereas TTF is one of the most distinguished organic molecules that behaves as an electron donor [37], which is widely employed in molecular electronics and charge-transfer systems. These analytes provide ideal probes for examining adsorption mechanisms, charge transfer, and molecular electronic modulation in nanosensing materials, since they exhibit distinct electron-withdrawing and electron-donating properties. In this work, first-principles density functional theory (DFT) investigations were carried out to evaluate the capability of the suggested hexagonal-like carbon nanocage, hereafter referred to

as *h*-LCNC, obtained using the sculpture method, for selective sensing of three different organic molecules, namely BZ, TCNE, and TTF. The sensing response of the *h*-LCNC, shown in Figure 1(c,d), towards BZ, TCNE, and TTF analytes is systematically investigated through structural relaxation, adsorption energy (E_{ads}), charge transfer (Ch_{Tr}), density of states (DOS), local density of states (LDOS), and finally, recovery time (τ) analysis. This work aims to explicate the sensing mechanism and evaluate the capability of the *h*-LCNC as a selective nanosensor for the identification of the neutral (BZ), electron-acceptor (TCNE), and electron-donor (TTF) molecules.

2. Computational Tools

All relaxed structures, the bare *h*-LCNC and the combined systems were obtained using the SIESTA [38] implementation of density functional theory (DFT), alongside the generalized gradient approximation in the formulation of Perdew-Burke-Ernzerhof (GGA-PBE) for the exchange-correlation functional [39]. GGA-PBE is extensively used to predict relaxed structures and electronic properties, charge transfer, adsorption energies, and associated electronic trends in first-principles sensing investigations [39-43]. For each molecule, several initial adsorption positions and orientations were considered before structural relaxation. The relaxed structures shown in this study correspond to lowest energy adsorption geometries obtained from these calculations. Then the most stable combined structure was chosen for all subsequent calculations. Double zeta polarized (DZP) basis sets together with norm-conserving pseudopotentials were used to represent the core electrons. All calculations were performed using a real-space integration with mesh cutoff energy of 300 Ry. A 60 Å vacuum was applied along X and Y directions, whereas periodic boundary conditions were applied along the Z direction. The periodic boundary conditions along the Z direction were applied because the *h*-LCNC was obtained using the sculpture method, where the initial bilayer graphene nanoribbon is sculpted as a one-dimensional periodic structure prior to spontaneous structural reconstruction into the final relaxed *h*-LCNC nanosensor. A Monkhorst-Pack k-point mesh of $1 \times 1 \times 30$ was employed for Brillouin zone integration in the DOS and LDOS calculations. The bare *h*-LCNC and all adsorption complexes were completely relaxed until the maximum force on each atom was less than $0.01 \text{ eV}\text{\AA}^{-1}$. To calculate the E_{ads} for each analyte adsorbed on the *h*-LCNC surface, as well as to determine the most energetically favorable adsorption complex, we used the following equation, which accounts for the basis-set superposition error (BSSE) [44, 45]:

$$E_{\text{ads}} = E_{(h\text{-LCNC}+\text{Analyte})} - E_{h\text{-LCNC}} - E_{\text{Analyte}} \quad (1)$$

where $E_{(h\text{-LCNC}+\text{Analyte})}$ is the total energy of the *h*-LCNC with the adsorbed analyte, $E_{h\text{-LCNC}}$ denotes the total energy of the *h*-LCNC nanosensor in the presence of the ghost atoms of the analyte, and E_{Analyte} indicates the total energy of the analyte in the presence of the ghost atoms of the *h*-LCNC nanosensor.

3. Electronic Structural of the *h*-LCNC

To obtain the proposed *h*-LCNC nanosensor, we began by sculpting the selected hexagonal-like shape, shown in Figure 1(a,b), from an AA-stacked graphene bilayer and allowing the carved shape to reconstruct spontaneously, forming the final relaxed *h*-LCNC

nanosensor composed entirely of stable sp^2 -bonded carbon atoms, as shown in Figure 1(c,d). The relaxed h -LCNC nanosensor has a highly symmetric closed nanocage geometry and contains non-hexagonal rings that are naturally formed during the global reconstruction, contributing to the structural stability of the final h -LCNC nanosensor. The non-hexagonal rings, consisting of a sp^2 -bonded network, are intrinsic to unique nanostructures obtained utilizing the sculpture method, distinguishing them from traditional fullerenes and pristine carbon nanotubes [7, 27-29, 46, 47].

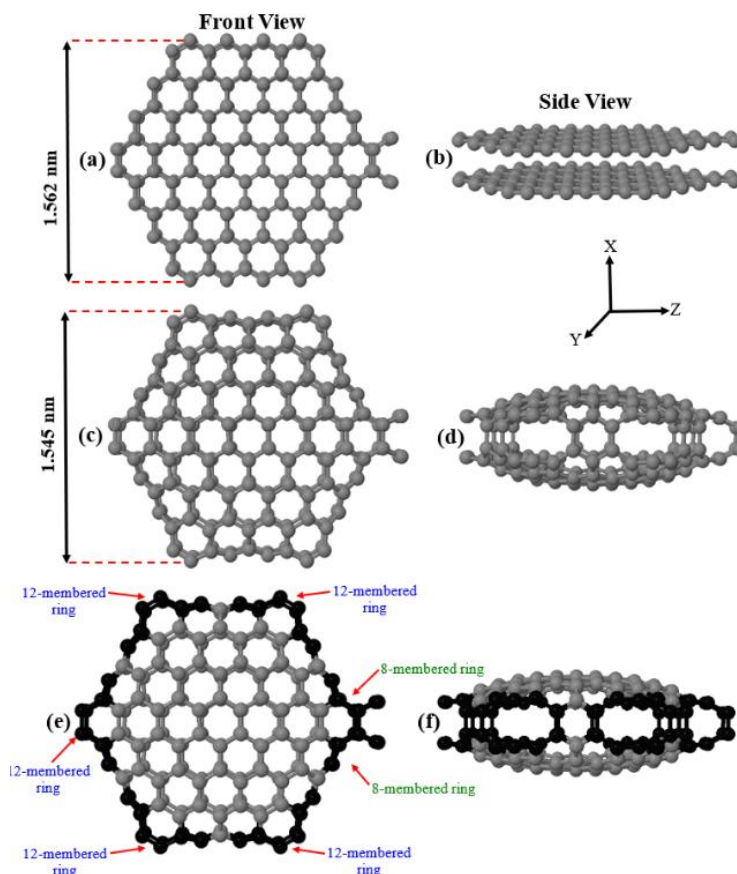


Figure -1 Front and side views of (a,b) Unrelaxed AA-stacked bilayer graphene, whose shape is similar to a hexagon. (c,d) The relaxed h -LCNC nanosensor. (e,f) The non-hexagonal rings formed in the h -LCNC nanosensor, consisting of five 12-membered rings and two 8-membered rings (highlighted in black). The structure is isolated in the YX plane, while is periodic along the Z direction.

To understand the electronic behavior of the bare h -LCNC, we calculate the electronic density of states (DOS) as shown in Figure 2. The obtained DOS shows that the h -LCNC has an energy gap of 0.764 eV, indicating that the bare h -LCNC acts as a semiconducting nanomaterial. This observed electronic behavior of the bare h -LCNC arises from the absence of the electronic states around the E_F [48, 49]. As can be seen from Figure 2, the occupied valence band (OVb) is positioned below the E_F and extended up to -0.377 eV, means $OVb \leq -0.377$ eV, whereas unoccupied conduction band (UCB) starts at +0.387 eV (i.e. $UCB \geq +0.387$ eV). The energy difference between the OVb and the UCB limits corresponds to the

calculated E_g of the bare h -LCNC (0.764 eV). Moreover, the sharp DOS peaks that observed above +0.387 eV and below -0.377 eV indicate the presence of localized electronic states emerging from the component atomic orbitals [48] of the bare h -LCNC nanosensor. Later, the DOS of the h -LCNC will be used as comparative reference for the adsorption complexes.

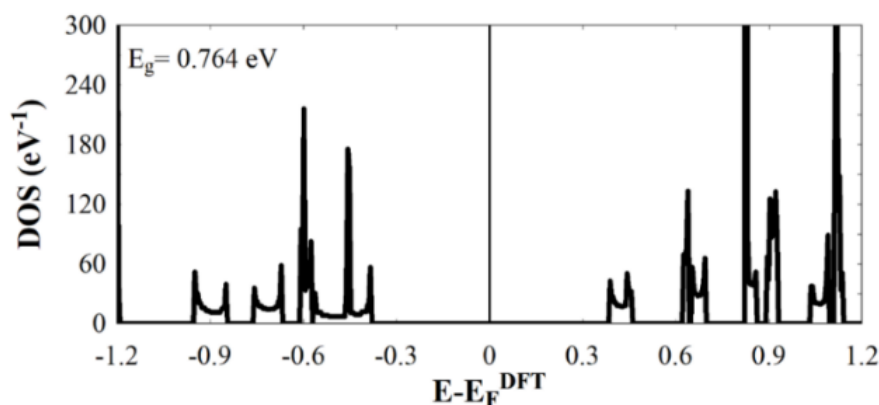


Figure -2 DOS of bare h -LCNC with an energy gap of 0.764 eV. The E_F^{DFT} denotes the Fermi energy predicted by the DFT and is shifted at 0 eV for conventional.

Figure 3 represents the schematic diagram of the relaxed structures of the targeted analytes, which are BZ, TCNE, and TTF (Figure 3(a-c)), the bare h -LCNC shown in Figure 3d, and their corresponding adsorption complexes, as shown in figure 3(e-g). The relaxed adsorption configurations obtained after fully geometric relaxation were used as a basis for following electronic structure calculations and selective sensing performance of the h -LCNC nanosensor.

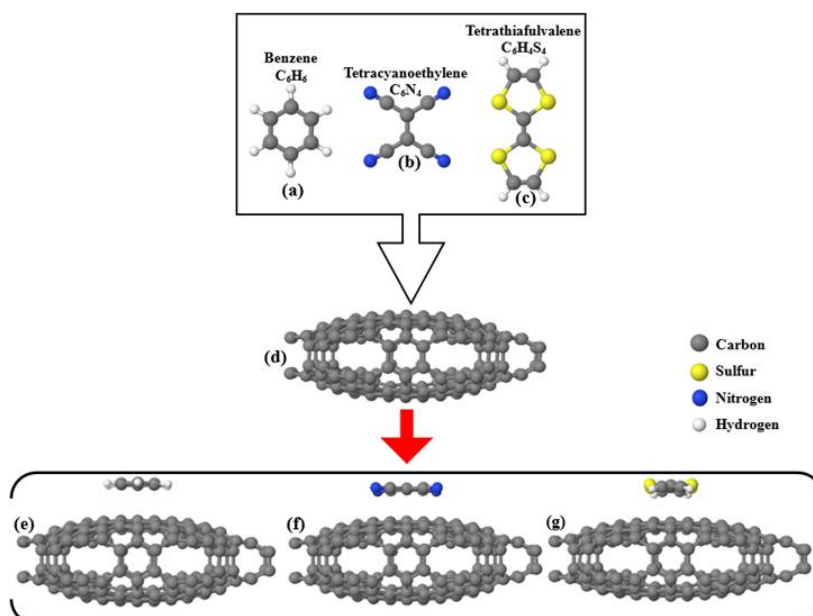


Figure -3 Relaxed molecular structures of the adsorbed molecules and their corresponding geometries on the h -LCNC surface. (a-c) Benzene (BZ, C_6H_6), Tetracyanoethylene (TCNE, C_6N_4), and Tetrathiafulvalene (TTF, $C_6H_4S_4$), respectively. (d) relaxed bare h -LCNC. (e-g) BZ@ h -LCNC, TCNE@ h -LCNC, and TTF@ h -LCNC, respectively.

4. Sensing Performance of the *h*-LCNC Nanosensor

Here, we investigate the sensing capability of the *h*-LCNC nanosensor toward the targeted molecules (BZ, TCNE, and TTF). To demonstrate this, we calculate the DOS of the adsorption complexes, namely BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC, as shown in Figure 4. From Figure 4, we can clearly see that the adsorbed molecules significantly influence the DOS of the bare *h*-LCNC, leading to non-trivial modifications in its electronic structure. Figure 4(a) shows that the adsorption of BZ on the *h*-LCNC reduces the E_g from 0.764 eV to 0.515 eV. On the other hand, the resulting E_g for the TCNE@*h*-LCNC is 0.577 eV, as shown in Figure 4(b). In contrast, Figure 4(c) shows that the adsorption of TTF on the *h*-LCNC surface decreases the E_g of the bare *h*-LCNC from 0.764 eV to 0.000 eV; *i.e.* TTF@*h*-LCNC exhibits metallic behavior. These results confirm the capability of the *h*-LCNC for the selective sensing of the BZ, TCNE, and TTF molecules.

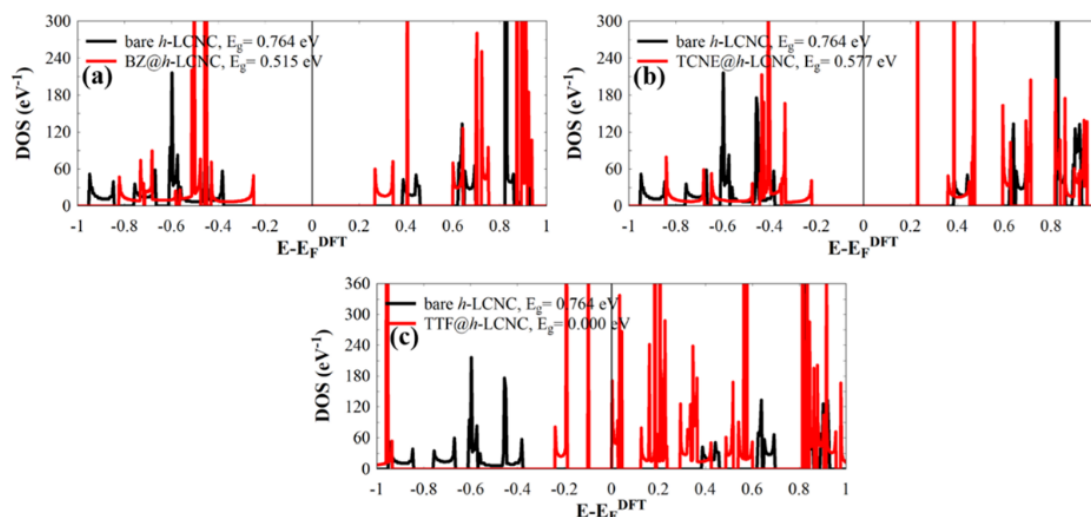


Figure -4 DOS of the BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC, DOS of the bare *h*-LCNC shown in black.

To gain more insight into the electronic structure of the *h*-LCNC and understand the origin of the electronic structure changes occurring due to the adsorption of the analytes on the *h*-LCNC surface, we investigate the local density of states (LDOS), as shown in Figure 5. For each adsorption complex, three energy windows were selected to represent the occupied states region below the E_F , the states region around the E_F , and the unoccupied states region above the E_F . In particular, the three selected energy windows for the bare *h*-LCNC are $-0.377 \text{ eV} \leq E-E_F \leq +0.387 \text{ eV}$, $-1.0 \text{ eV} \leq E-E_F \leq -0.377 \text{ eV}$, and $+0.387 \text{ eV} < E-E_F < +1.0 \text{ eV}$. For the BZ@*h*-LCNC, the three selected energy windows are $-0.252 \text{ eV} \leq E-E_F \leq +0.263 \text{ eV}$, $-1.0 \text{ eV} < E-E_F < -0.252 \text{ eV}$, and $+0.263 \text{ eV} < E-E_F < +1.0 \text{ eV}$. Similarly, the three selected energy windows for the TCNE@*h*-LCNC are $-0.221 \text{ eV} \leq E-E_F \leq +0.365 \text{ eV}$, $-1.0 \text{ eV} < E-E_F < -0.221 \text{ eV}$, and $+0.365 \text{ eV} < E-E_F < +1.0 \text{ eV}$. Finally, for TTF@*h*-LCNC, the three selected energy windows are $-0.10 \text{ eV} \leq E-E_F \leq +0.10 \text{ eV}$, $-1.0 \text{ eV} < E-E_F < -0.10 \text{ eV}$, and $+0.10 \text{ eV} < E-E_F < +1.0 \text{ eV}$. The obtained LDOS results for the bare *h*-LCNC and BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC complexes demonstrate that the adsorbed analytes (BZ, TCNE, and TTF) perturb the distribution of the electronic states around E_F through orbital interactions between

the *h*-LCNC surface and the adsorbed molecules. These interactions become stronger for the TTF adsorption, which leads to the disappearance of the E_g and the emergence of metallic behavior, which agrees with the DOS results.

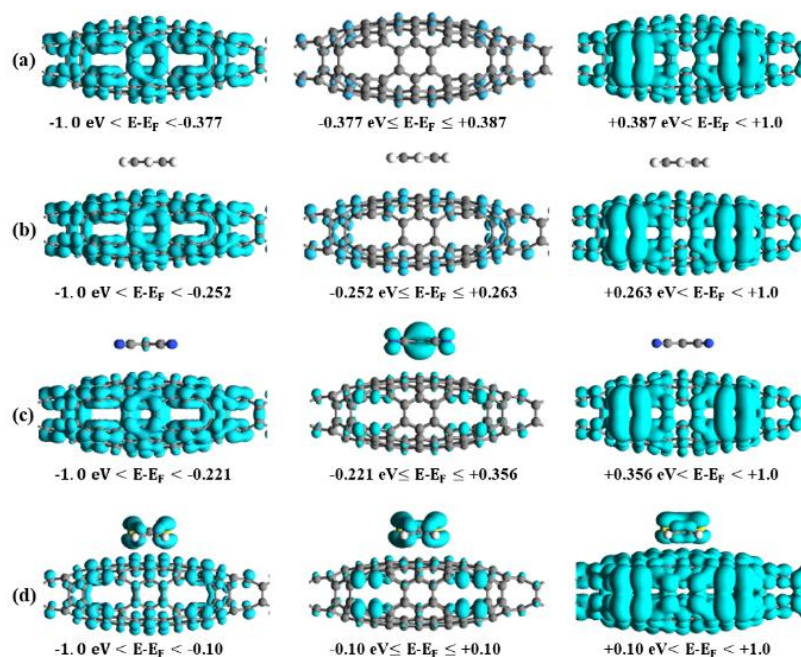


Figure -5 LDOS for the bare *h*-LCNC and BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC. (a) The bare *h*-LCNC for three energy ranges, $-0.377 \text{ eV} \leq E - E_F \leq +0.387 \text{ eV}$ (around E_F), $-1.0 \text{ eV} \leq E - E_F \leq -0.377 \text{ eV}$ (below E_F), and $+0.387 \text{ eV} < E - E_F < +1.0 \text{ eV}$ (above E_F). (b) The BZ@*h*-LCNC for three energy ranges, $-0.252 \text{ eV} \leq E - E_F \leq +0.263 \text{ eV}$ (around E_F), $-1.0 \text{ eV} < E - E_F < -0.252 \text{ eV}$ (below E_F), and $+0.263 \text{ eV} < E - E_F < +1.0 \text{ eV}$ (above E_F). (c) The TCNE@*h*-LCNC for three energy ranges, $-0.221 \text{ eV} \leq E - E_F \leq +0.365 \text{ eV}$ (around E_F), $-1.0 \text{ eV} < E - E_F < -0.221 \text{ eV}$ (below E_F), and $+0.365 \text{ eV} < E - E_F < +1.0 \text{ eV}$ (above E_F). (d) The TTF@*h*-LCNC for three energy ranges, $-0.10 \text{ eV} \leq E - E_F \leq +0.10 \text{ eV}$ (around E_F), $-1.0 \text{ eV} < E - E_F < -0.10 \text{ eV}$ (below E_F), and $+0.10 \text{ eV} < E - E_F < +1.0 \text{ eV}$ (above E_F).

To evaluate which adsorption complex is the most energetically favorable, we investigate the stability of the BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC by calculating the adsorption energy (E_{ads}) using Equation (1), as shown in Table 1. The adsorption energies listed in Table 1 indicate that the all-adsorption complexes have negative values, implying that the BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC complexes are energetically favorable. TTF shows the most negative adsorption energy, with a value of -1.202 eV , indicating its strongest interaction with the *h*-LCNC, followed by TCNE with an adsorption energy of -1.142 eV , whereas BZ shows the weakest interaction with the *h*-LCNC, with an adsorption energy of -0.715 eV . For further insight into the electronic behavior of the adsorption systems, we estimate the charge transfer (Ch_{Tr}) between the *h*-LCNC and the targeted adsorbed molecules using Mulliken charge population analysis, as shown in Table 1. The tabulated Ch_{Tr} results confirm the different electronic interactions between the targeted adsorbed analytes and the surface of the *h*-LCNC nanosensor. From Table 1, we can see that BZ and TCNE have negative Ch_{Tr} values, indicating that these molecules withdraw electrons from the *h*-LCNC nanosensor, while TTF has a positive Ch_{Tr} value; *i.e.*, TTF, with the highest Ch_{Tr} value, donates electrons to the *h*-LCNC nanosensor.

Table 1- E_{ads} , Ch_{Tr} , and τ for BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC. The Ch_{Tr} is in electrons per molecule (q). Negative values of Ch_{Tr} indicates that the molecule receives charge from the *h*-LCNC.

STRUCTURE	E_{ads} (eV)	Ch_{Tr} (q)	τ @300 K (s)	τ @400 K (s)	τ @500 K (s)
BZ@ <i>h</i> -LCNC	- 0.715	- 0.051	1.027×10^0	1.020×10^{-3}	1.610×10^{-5}
TCNE@ <i>h</i> -LCNC	- 1.142	- 0.315	1.530×10^7	2.447×10^2	3.242×10^{-1}
TTF@ <i>h</i> -LCNC	- 1.202	0.354	1.559×10^8	1.395×10^3	1.305×10^0

To have a look at the regeneration of the *h*-LCNC nanosensor, we finally calculate the recovery time (τ) at various temperatures (300, 400, and 500 K) for the BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC systems, as shown in Table 1. The calculated τ results show that the τ significantly decreases as the temperature increases from 300 K to 500 K for all adsorption complexes. At 300 K, the BZ@*h*-LCNC complex shows the shortest τ (1.027×10^0 s), while the TCNE@*h*-LCNC and TTF@*h*-LCNC complexes display longer τ with values of 1.530×10^7 s and 1.559×10^8 s, respectively. TTF@*h*-LCNC shows the longest τ due to its strongest adsorption. Increasing the temperature to 400 K leads to a dramatic decrease in the τ values to 1.020×10^{-3} s, 2.447×10^2 s, and 1.395×10^3 s for the BZ@*h*-LCNC, TCNE@*h*-LCNC, and TTF@*h*-LCNC complexes, respectively. An additional decrease occurs when the temperature is increased to 500 K, with the τ values dropping to 1.610×10^{-5} s, 3.242×10^{-1} s, and 1.305×10^0 s, implying that increasing the operating temperature enables the desorption of the adsorbed molecules and considerably enhances the regeneration of the *h*-LCNC nanosensor. Overall, the calculated factors, namely the DOS, LDOS, adsorption energy, charge transfer, and recovery time, together demonstrate that the proposed *h*-LCNC nanosensor has excellent selective sensing performance toward the targeted molecules (BZ, TCNE, and TTF).

5. Conclusions

We have demonstrated that the carbon nanocage constructed using the sculpture method provides a comprises platform for selective sensing of three different types of organic molecules (BZ, TCNE, and TTF). Upon the structural relaxation, the nanocage remains structurally stable and has of two exposed adsorption surfaces with a small energy gap of 0.764 eV, confirming its semiconducting behavior appropriate for sensing applications. The calculated adsorption energies revealed that all adsorption systems are energetically favorable, with TTF interacting most strongly with the *h*-LCNC surface, followed by TCNE and BZ. Charge transfer analysis indicated distinct electron transfer properties, with BZ and TCNE acting as electron acceptors by withdrawing electrons from the *h*-LCNC nanosensor, while TTF acts as an electron donor to the *h*-LCNC nanosensor. The DOS and LDOS results showed that the adsorption of the targeted analytes on the *h*-LCNC surface significantly changed the electronic structure of the *h*-LCNC nanosensor ($E_g = 0.764$ eV). Specifically, BZ decreases the energy gap to 0.515 eV, TCNE generates a smaller reduction to 0.577 eV, while TTF entirely removes the energy gap, resulting in a transition from semiconducting to metallic behavior. These distinct electronic responses enable obvious differentiation among the targeted molecules. Additionally, the calculated recovery times decreased considerably with increasing operating temperature, demonstrating that the regeneration of the *h*-LCNC nanosensor can be accomplished effectively under elevated operating temperature conditions. As a result, the calculated factors, namely the DOS, LDOS, E_{ads} , Ch_{Tr} , and τ , demonstrate that the suggested *h*-LCNC nanosensor exhibits excellent selective sensing capability toward the investigated analytes (BZ, TCNE, and TTF). Under practical operating conditions, external environmental factors, such as the surrounding medium, solvent, and humidity, may impact the adsorption and electronic responses of the proposed *h*-LCNC nanosensor, which may modify its electronic behavior. Therefore, the present findings represent the intrinsic sensing properties of the nanosensor, providing a theoretical basis for future experimental investigations under real-life conditions.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Laith A. Algharagholy and Zainab H. Almousawi acknowledge the Iraqi Ministry of Higher Education and Scientific Research and University of Sumer for the support.

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