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Research paper

First-principles investigation on switching properties of spiropyran and merocyanine grafted graphyne nanotube device

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ABSTRACT

The density functional theory (DFT) method with non-equilibrium Green's function (NEGF) method is used to study the electronic properties of the graphyne nanotube device. The graphyne nanotube is used as a base material to graft photochromic spiropyran and merocyanine molecules. The current voltage characteristics clearly give the insights on the switching properties of spiropyran and merocyanine grafted graphyne device. The findings show that spiropyran grafted graphyne device as ON state and merocyanine grafted graphyne device as an OFF state device. Moreover, upon shining light of proper wavelength, the spiropyran/merocyanine grafted graphyne nanotube device can be used as a switch.

1. Introduction

Carbon exhibits different hybridized states (*sp*, sp^2, sp^3) in their diverse allotropes like graphene, fullerenes, etc., Although, graphene, a 2-D atomic layer of sp^2 bonded carbon atoms has acquired a vast attention due to its exclusive mechanical and electronic properties like Dirac cone, it has its own drawback in high speed switching devices [1]. Graphyne, an allotrope of carbon with one atom thick planar sheet of *sp* and sp^2 bonded carbon atoms is a modification of graphene that has acetylenic linkages connecting the hexagons of graphene. The original honeycomb lattice of graphene has been shattered with the existence of *sp* carbon atoms in case of graphyne. Graphyne possesses natural semiconducting characteristics and are potentially remarkable in directional electrical conductivity [2].

Four types of graphyne namely α-, β-, γ- and 6, 6, 12- graphynes have been reported [2,3]. In 1987, Baughman et al. proposed graphyne as a part of a new structure of carbon that had been sparingly reported [3]. First-principles electronic structure calculations revealed that graphynes produce small carrier effective masses and high carrier mobility [4]. In addition, peculiar optical properties like high third-order nonlinear optical susceptibility, strong anisotropic optical observation and high fluorescence efficiency are envisioned. It retains appealing mechanical properties like softening nature with increase in temperature. Zhang et al. investigated graphyne using molecular dynamics (MD) with Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [5]. Moreover, the reduction in fracture stress and Young's modulus are observed due to the existence of acetylenic linkages [5]. The adsorption of transition metals on the graphyne sheets has great impact in their overall behavior [6]. Furthermore, in 2008, Haley demonstrated the synthetic strategies and optoelectronic properties of graphyne based on dehydrobenzo annulene framework [7]. Later on, the synthesis of graphyne on metal surfaces has been reported, which is synthesized by chemical vapor deposition of organic precursor. The properties of graphyne support wide applications, which are used in chemical sensors, anisotropic conductors, semiconductor metal hybrids, etc. The flow of electrons in graphyne is remarkably faster and is unidirectional in nature, making it possible application in the electronic components. Peng et al. reported about the quasistatic method to arbitrate the elastic constants of graphyne using density functional theory (DFT) [8].

Compounds generally encounter an isomerisation transition resulting in changes in their structural and electronic composition when a foreign stimulus acts on it. It is well known that spiropyran molecules are photochromic in nature. The photochemical reaction results in two species namely spiropyran (closed ring isomer) and merocyanine (open ring isomer). Upon irradiation of UV light with a wavelength of 365 nm, spiropyran undergoes a ring opening transition resulting in colored cis and trans forms of merocyanine. Further, merocyanine can be reversed to colorless spiropyran thermally or by irradiation with visible light of wavelength ≥500 nm. [9]. Spiropyran and merocyanine have different physio chemical

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properties. The spiropyran molecule consists of an indoline and chromene component combined together through a spiro junction and oriented perpendicular to each other, whereas merocyanine shows a single delocalized transition shift resulting in an extended π- conjugation between indoline and chromene component. The photochemical isomerization makes way to alter the electronic and optical properties by changing the switching state. Besides, due to their high sensitivity to the environmental factors, spiropyran have found their application in ionic and pH sensors. They have also found various applications in the photocontrolled drug delivery, non-linear optics, molecular electronics, bio imaging, which act as an easily tunable molecular switch.

Till date, most of the previously reported work is chiefly engaged with the electronic, optical and mechanical properties of graphyne. To our knowledge, attention has been given to the effect of acetylenic linkages on the transmission spectrum, current voltage characteristics of graphyne (i.e., isolated graphyne nanotube). We present the consequence of spiropyran and merocyanine anchored on graphyne nanotube and their combined effect on the current voltage characteristics, their switching behavior between ON and OFF states in the present report.

2. Computational details

The first-principles studies on graphyne nanotube molecular device is explored using density functional theory (DFT) with non-equilibrium Green's function (NEGF) method using Tran-SIESTA module in SIESTA package [10]. The electron-electron interaction between the graphyne and spiropyran and merocyanine molecules are studied using generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [11–13]. The structure of graphyne nanotube was fully optimized with the Brillouin zone k-point mesh of $1 \times 1 \times 10$. In order to study the band structure of graphyne nanotube the k-point mesh is increased to $1 \times 1 \times 100$. Since the graphyne nanotube molecular device has been constructed along z-axis, a dense k-point sampling is taken along the z-axis, while constructing the device. Moreover, graphyne nanotube is optimized by reducing the atomic forces between the atoms in graphyne nanotube are achieved below 0.05 eV/Å. The electronic wave functions of graphyne nanotube are analyzed in term of basis set that depends on numerical orbitals. The double zeta polarization (DZP) basis set is utilized while optimizing graphyne nanotube device [14,15]. The atoms are allowed in the graphyne nanotube to freely move along with their positions till the convergence force below 0.05 eV/Å is obtained. To avoid the interaction of periodic images a vacuum padding of 10 Å along x and y axes is used.

3. Results and discussions

3.1. Structure of graphyne based molecular device

Initially, graphyne nanosheets are designed and graphyne sheets are folded to form graphyne nanotube. The graphyne nanotube base material is designed as a two-probe system. The supercell of the graphyne nanotube is $1 \times 1 \times 6$. The structural stability of graphyne nanotube is calculated using formation energy as shown in equation below

$$E_{Form} = 1/n\,[E_{Total} - nE(C)]$$

where E_{Total} represents the total energy of graphyne nanotube. E(C) refers the energy of isolated carbon atom and n is the total number of atoms in graphyne nanotube. The formation energy of graphyne nanotube in the present work is observed to be −7.72 eV. The negative magnitude of the formation energy of the graphyne base material clearly confirms the stability of the designed graphyne base material. The graphyne nanotube is divided into three regions viz. left probe, scattering region and right probe. Among, which the scattering region consists only of carbon atoms with their acetylenic linkages. The operating voltage is an important aspect regarding the design of molecular device. In the proposed system the operating bias voltage is found to be optimum in the voltage range of 0–5 V. Besides, beyond this operating voltage, the scattering region gets deteriorated and molecular device becomes an open circuit. The electronic properties of the graphyne nanotube molecular device are studied using device density of states and transmission spectrum. In addition, spiropyran and merocyanine molecules are anchored on the graphyne nanotube device and the switching properties of anchored spiropyran and merocyanine are studied and the results are reported. As mentioned earlier, the conversion of spiropyran photochromic molecule to merocyanine photochromic molecule starts with the cleavage of the C—O bond, which then involves two localized transitions viz., π-π∗ electronic transition in the indoline part and another one in the chromene moiety. Fig. 1a. represent the schematic diagram of isolated graphyne nanotube. Figs. 1b and 1c illustrates the schematic diagram of spiropyran and merocyanine anchored graphyne nanotube. In Figs. 1b and 1c, both spiropyran and merocyanine are grafted to the graphyne nanotube by means of NO_2. (*The co-ordinates for graphyne nanotube is given in the Supplementary Information for the readers to carry out further studies*)

3.2. Energy band structure and density of states of graphyne nanotube

The density of states infers the distribution of states as a function of energy and provides perception about transport phenomena and electronic structure of graphyne nanotube [16–18]. The density of charge for various energy intervals of graphyne nanotube is envisioned by device density of states (DDOS) spectrum. In zero bias condition, the energy band structure of isolated graphyne nanotube is shown in the Fig. 2. Moreover, the energy band gap of isolated graphyne nanotube is calculated to be 0.19 eV along the gamma (**Γ**) point. The energy band gap can be fine-tuned with the geometry of graphyne nanotube. Fig. 3 depicts the density of states (DOS) spectrum of isolated graphyne base material. Further, the peaks are noticed within the energy interval of −5 eV to 5 eV in the occupied and virtual orbitals. Figs. 4a, 4b and 4c illustrates the DDOS spectrum of isolated, spiropyran and merocyanine grafted graphyne nanotube device. Moreover, for zero bias conditions, the peaks are observed near to the Fermi level, which arose due to the mismatch between the electronic chemical potential

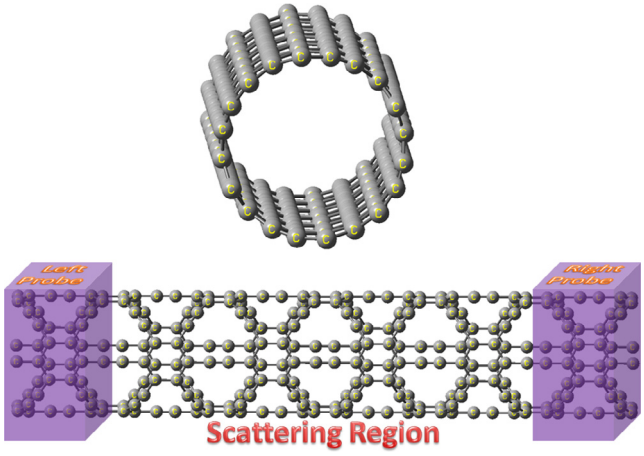

Fig. 1a. Schematic diagram of isolated graphyne nanotube molecular device.