COMPUTATIONAL MODELLING OF CELLULOSE AND CARBON-BASED NANOWIRES USING FIRST PRINCIPLES DENSITY FUNCTIONAL THEORY

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ABSTRACT

Nanomaterials play very important role in nanotechnology. Conducting investigations about their properties and applications require standard computational models that mimic their physical aspects. In this, paper, we designed a nanowire model of cellulose and carbon-based nanomaterials (H-doped CNT) with the aid of first-principles Density Functional Theory. All the structures were optimized until the convergence criterion of 10^{-08} au is reached. We made sure that the ionic forces between atoms are small enough in accordance with the Hellman-Feynman Theorem. For the cellulose, only two polymerizations with 12 C atoms, 20 H atoms and 10 O atoms are considered, forming a cellulose unit. We have seen that its structure is formed via beta-glycosidic bonds. For the carbon-based nanomaterial, we generated a pristine (9,9) carbon nanotube (CNT) and introduced substitutional H doping, making it an H-doped CNT. All the structures where then meshed, forming nanowires. This paper is designed for future researchers about the modelling of nanostructures.

Keywords: Nanomaterials, nanotechnology, nanowire, nanocellulose, carbon-based nanomaterial, Density Functional Theory, Hellman-Feynman Theorem

INTRODUCTION

Nanomaterials [2, 3, 4, 9, 10, 19, 21] are some of the very interesting and widely studied nowadays due to their contributions to science. These materials have extraordinary and varying properties depending on how they are made. For instance, nanopolymers are known to have enormous impacts for their applications in human health [4], nanofluids [24], and tissue engineering [15].

Shanmuganathan, R., et.al [23] conducted a review about Chitosan nanopolymers and their roles as drug carriers to treat cancer cells. Accordingly, Chitosan nanopolymers could potentially be used in different treatment techniques. As known, cellulose is the most abundant and most common natural polymer [12]. Many studies were conducted that focused on the contributions that nanocellulose has for nanotechnology. Some of its applications [11, 12] include energy storage applications and electronics, among others.

Since the discovery of graphene [16, 17], the search for other nanomaterials continuously grows. Aside from nanopolymers, carbon-based nanomaterials have become subjects of interest for many scientists and engineers. Carbon nanotubes (CNTs) (see Figure 1) are tiny cylinder of carbon-based nanomaterial which could be imagined as a rolled graphene. Some of their contributions in nanotechnology include the electrochemical and electronic applications [1], gas sensing applications [7], and biomedical applications [22]. With the abovementioned characteristics and applications of these nanomaterials, providing models that could match their real applicability is thus very important.

In this work, we create a model that mimics a cellulose and defected carbon nanotube nanowires with the aid of first-principles Density Functional Theory (DFT). This paper provides the details on how these nanomaterials are dealt computationally.

(a) (b) (c)

Figure 1. **S**tructure of armchair single-walled carbon nanotube. (a) Top, (b) side and (c) tilted views.

COMPUTATIONAL DETAILS

In this research, we implement the first-principles calculations [3, 19] for the optimization of the structures in Quantum Espresso. We make use of the Generalized-gradient Approximation [6] as our implementing exchange-correlation functional of the form

$$E_{XC}^{GGA}[\rho_{\uparrow},\rho_{\downarrow}] = \int d^3 r f(\rho_{\uparrow},\rho_{\downarrow},\nabla\rho_{\uparrow},\nabla\rho_{\downarrow}) \quad (1)$$

which deals with the gradient of the local density. It was adopted with the Perdew-Burke-Ernzerhof (PBE) together with the (DFT-D3) correction [14, 18] to describe the van der Waals interactions for non-local dispersion forces [13].

As known, when the energy is found, the ionic forces could be straightforwardly calculated using the famous Hellman-Feynman theorem [8, 20] of the form:

$$F_I = \frac{\partial E(R)}{\partial R_I} = \left\langle \Psi \left| \frac{\partial E(R)}{\partial R_I} \right| \Psi \right\rangle \quad (2)$$

$$F_I = -\int \rho_R(r) \frac{\partial V_R(r)}{\partial R_I} - \frac{\partial E_N(R)}{\partial R_I} \quad (3)$$

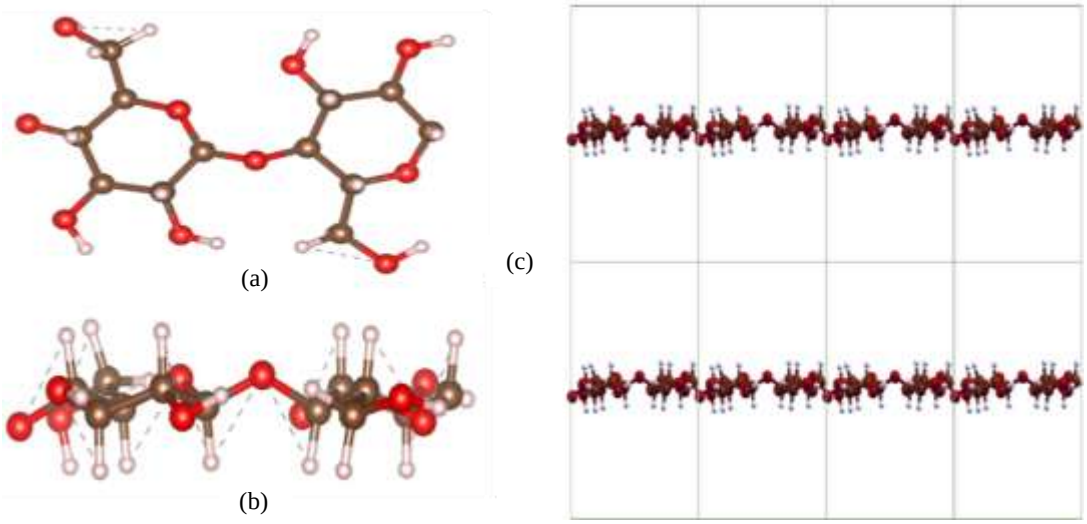
where the electron-nucleus interaction and the electrostatic ion-ion interaction depend only on the ionic position.

RESULTS AND DISCUSSIONS

After constructing the structure of the nanocellulose $(C_6H_{10}O_5)_n$ and H-doped CNT, we performed structural optimizations until the convergence criterion of 10^{-08} au is satisfied. The results are the following.

Structure of $(C_6H_{10}O_5)_2$

Accordingly, a cellulose $(C_6H_{10}O_5)_n$ is a long chain of glucose monomers, connected by beta-glycosidic-bonds. In this research work, only two polymerizations or glucose monomers are considered with 12 carbon (C) atoms, 20 Hydrogen (H) atoms and 10 Oxygen (O) atoms.



(b)

Figure 2. (a) Front and side view of cellulose unit, and (c) the cellulose nanowire. Atom colors: Brown – Carbon, White – Hydrogen, Red – Oxygen.

Figure 2a and Figure 2b represent the front and side views of the optimized $(C_6H_{10}O_5)_2$, respectively. As seen, the two monomers are connected by flipping the second monomer, allowing a beta-glycosidic bond. We then mesh this nanopolymer towards the lattice vector c (z-axis) to form a nanowire. Figure 2c is a 1x2x4 representation of a cellulose nanowire. Clearly, we can view it as a repeated cellulose unit (cellulose chain) as seen in Figure 2b. It should be noted that we can always extend the nanowire by defining the z component of the mesh, such that it is given by 1 x 1 x nk3.

Structure of H-Doped Carbon Nanotube

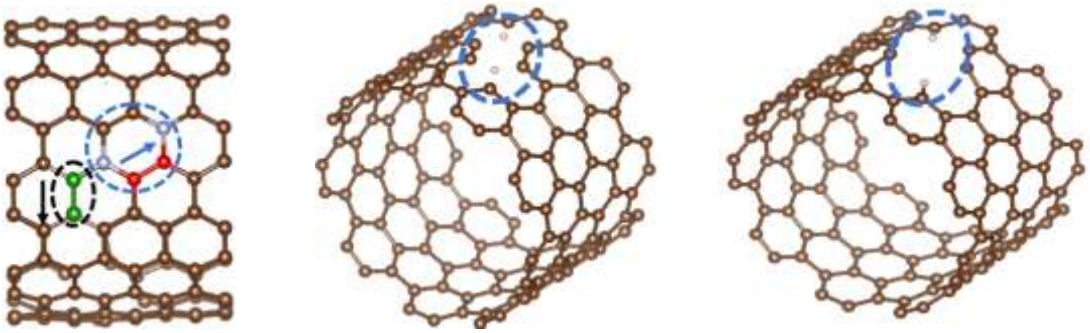
We generated four supercells of single-walled (9,9) CNT and modified the surface by introducing a divacancy. Table 1 shows the parameters of the considered CNT.

Table 1. Parameters of the generated CNT (9,9)

Lattice vector	Length (Å)
a	12.23159
b	12.23159
c	9.84496

In Figure 3a, we can see the different ways of making a divacant CNT [5], depending on the location of the depleted C atoms. As seen, we can have a tilted divacancy (blue dotted circle) and a perpendicular divacancy (black dotted circle) with respect to the tube axis. In this paper, we only considered the tilted divacancy. We then embedded two substitutional H atoms to replace the depleted C atoms, forming an H-doped CNT. Figure 3b

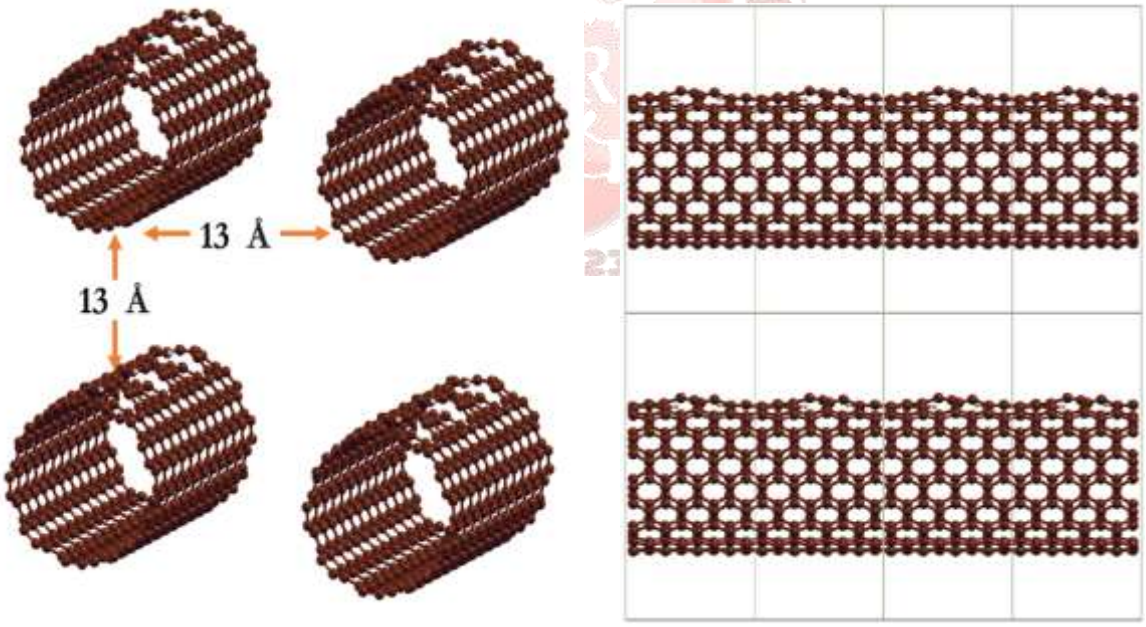
shows that there is no C-H bond formed for the unoptimized doped CNT. This could be attributed to the small size of the H atoms, relative to the C atoms. After full structural optimization, the H atoms bonded with the nearest C atoms as seen in Figure 3c.



(a) (b) (c)

Figure 3. (a) Side view of the pristine (9,9) CNT, and the tilted views of (b) unoptimized and (c) optimized H-doped CNT.

By considering a kpoint grid of nk1 x nk2 x nk3, we can form repeated supercells in all directions. In Figure 4, we can see that our doped CNT forms a nanowire that extends towards the z-axis. Designing this CNT is a practical method to mimic a carbon-based nanowire that will help us to accurately calculate the properties of interest.



(a) (b)

Figure 4. (a) Tilted view of the 2x2x3 supercells and (b) side view of the 1x2x4 supercells of H-doped CNT.

SUMMARY AND CONCLUSION

In this work, we designed a model of cellulose and H-doped CNT nanowires to see the representation of their atomic structures. We first generated the structures and optimized them in accordance with the Hellman-Feynman Theorem. The cellulose is designed with only two connected monomers by beta-glycosidic bonds. For the carbon-based nanomaterial, we generated a pristine (9,9) CNT and introduced a defect by H doping. We

observed that after structural optimization of the H-doped CNT, two C-H bonds were formed. We then let the structures form a nanowire by considering supercells. In all cases, this work may serve as a reference for future researchers in computational condensed matter physics.

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