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Exploring the Functionality of Cellulose Biopolymer as Carbon Nanotube Composite and Heavy Metals Adsorbent Material: Insights from First-Principles Calculations

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Abstract: Herein, using first-principles density functional theory, we explored the applicability of cellulose as a functional material of carbon nanotubes and as an adsorbent material for heavy metals (As, Hg, and Pb). The calculations revealed that cellulose is suitable for the non-covalent functionalization of SWCNT. The interaction of SWCNT with cellulose is mainly classified as physical interaction. This claim is supported by the results of binding energy, equilibrium distances, and charge transfer analysis of the SWCNT and cellulose. The electronic structure of the prototype SWCNT in the cellulose nanocomposite is well maintained, where no visible hybridization of the orbital characters is observed. The calculations explain experimental observations that cellulose is suitable for the non-covalent functionalization of SWCNT. Further calculations show that As and Pb can be trapped by cellulose biopolymer, while Hg indicates weak interaction. A significant reduction of the bandgap of cellulose is observed upon adsorption of As and Pb. These findings show cellulose can be used as an adsorbent sensing material for As and Pb. Overall, the results of this study confirm that cellulose is a promising functional material for SWCNT and a renewable adsorbent material for heavy metals.

Keywords: cellulose; carbon nanotubes; heavy metals; adsorption; functionalization; nanocomposite; density functional theory.

1. Introduction

The cellulose biopolymer $(C_6H_{10}O_5)_n$, the most abundant biopolymer on the planet, has paid much interest owing to its impressive mechanical properties, biocompatibility, and rich chemical properties [1–3]. Cellulose biopolymer is the building block of natural fiber. Thus, it can be extracted from various plants and even some organisms, making it a low-cost and renewable material [4–6]. The eco-friendliness, biodegradability, and mechanical properties of cellulose make it the preferred candidate to replace petroleum-based polymers. Moreover, owing to cellulose's strength, lightweight, low thermal expansion, and flexibility, it is used in conductive composites, photovoltaic applications, and adsorbent technology for water remediation technology [7–10]. The increasing number of research papers and patents on

cellulose-based materials reflect its importance for future engineering materials with advanced properties and associated eco-friendliness [11–13]. In particular, many reports show that cellulose is promising as a functional material for carbon nanotubes and heavy metals adsorbent material.

Carbon nanotubes (CNT) exist in bundles due to the van der Waals interaction between the nanotubes. Earlier reports revealed cellulose and its derivatives are effective functional dispersants of single-walled carbon nanotubes (SWCNT) and have broad applicability of the nanocomposite [4, 14, 15]. For example, Riou *et al*. [16] report that carboxymethyl cellulose can disperse SWCNT uniformly. Also, the paper of Deng *et al*. [17] reports the super capacitance properties observed in the carbon nanotube and cellulose composite. Moreover, CNT and cellulose hybrid materials show various functionality reported by multiple authors [18, 19]. For example, Ma *et al*. [20] were able to fabricate strong cellulose and carbon nanotube fiber with electrical heating and humidity-sensing properties. Wang *et al*. [19] were able to produce a robust filament that has 472.1 MPa that has strain and humidity sensor capabilities. Despite these reports, the wrapping mechanism of cellulose on carbon nanotubes is not fully understood and is still a subject of basic research for further optimization of cellulose – (SW)CNT composites.

Aside from composite material of carbon nanostructures, cellulose was extensively studied for water purification technology, particularly for heavy metals adsorbent. Heavy metals are one of the most common inorganic chemicals released into the environment from factories, chemical products, and agricultural waste [21, 22]. The typical heavy metals found in water are arsenic (As), antimony (Sb), cadmium (Cd), mercury (Hg), and lead (Pb) [21, 23]. Water intake with these heavy metals exceeding the permitted amount can significantly put a person at risk. For example, Pb, As, and Hg can cause damage to the nervous system, brain, skin, and lungs, even for a small amount (>10μg), and can be carcinogenic [24]. Thus, removing and detecting these heavy metals is crucial in securing the environment and human health. Cellulose biopolymer is particularly attractive for water purification adsorbent material due to its large surface area and anti-fouling behavior [11]. These important properties are further reflected in the number of reports of cellulose-based materials for water purification systems [11, 25, 26].

This study investigated the bonding mechanism of cellulose with the SWCNT and explored the adsorption ability of cellulose for trapping heavy metals. All calculations are conducted using first-principles density functional theory (DFT). The simulation revealed that cellulose is suitable for the non-covalent functionalization of carbon nanotubes, where it preserved the electronic structure of the carbon nanotube. The adsorption of As, Hg, and Pb revealed that As and Pb can strongly be adsorbed on the hydroxyl, hydroxymethyl, and cellulose backbone sites, while the Hg yields minimal binding energy in all studied configurations.

2. Materials and Methods

All DFT calculations are conducted using Quantum Espresso using a plane-wave basis set, PAW pseudopotential, PBE exchange-correlation functional, and Grimme-D3 dispersion correction [27–33]. The energy and charge cutoff is set to the standard value, 45 Ry and 330 Ry, respectively. The optimization calculation sets the energy and force convergence threshold to 10^{-8} Ry and 10^{-5} Ry /Bohr, respectively. The Γ-point algorithm optimizes Cellulose/SWCNT and Cellulose/Heavy-Metal atomic configurations. A 15 Å vacuum slab is included to remove

the interaction of the periodic images of studied systems. In the electronic structure calculations of SWCNT/Cellulose nanohybrid, a *1x1x11* k-points is used for the *SCF* calculations, and *1x1x30* k-points are used for the electronic density of states calculations for an accurate description of the electronic state's landscape.

3. Results and Discussion

The discussions are divided into two parts, section 3.1 and section 3.2. In section 3.1, the synergetic interaction of cellulose and SWCNT nanocomposite is evaluated by examining the binding energy, Charge Density Difference (CDD), Electron Localization Function (ELF), and electronic density of states. In section 3.2, the interaction of As, Hg, and Pb on different sites of cellulose is discussed by careful inspection of the bond lengths, binding energy, bandgap, and electronic density of Cellulose/Heavy-Metals atomic configurations.

3.1. SWCNT and cellulose nanocomposite.

Two cellulose chains are adsorbed on the prototype SWCNT(7,1), shown in Figure 1.

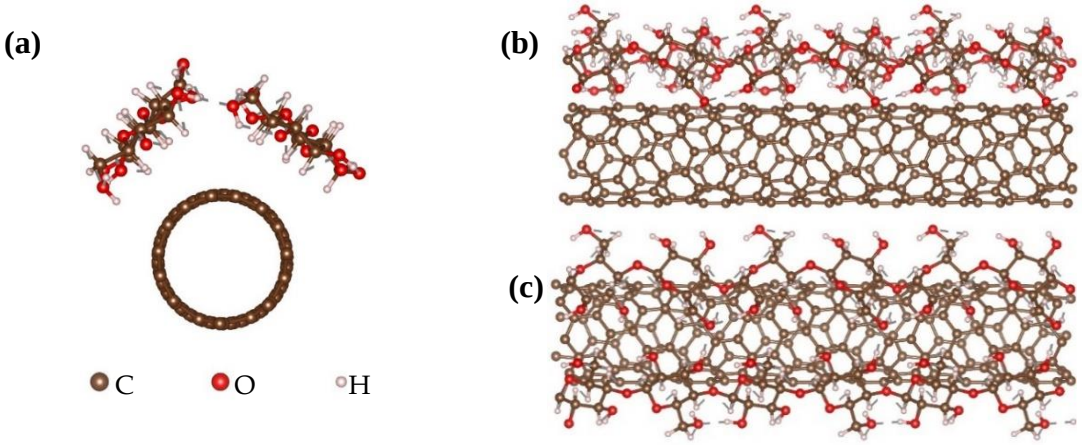

Figure 1. The optimized atomic configuration of SWCNT(7,1) and cellulose chains nanocomposite. **(a)** view from tube direction, **(b)** side view, and **(c)** top view.

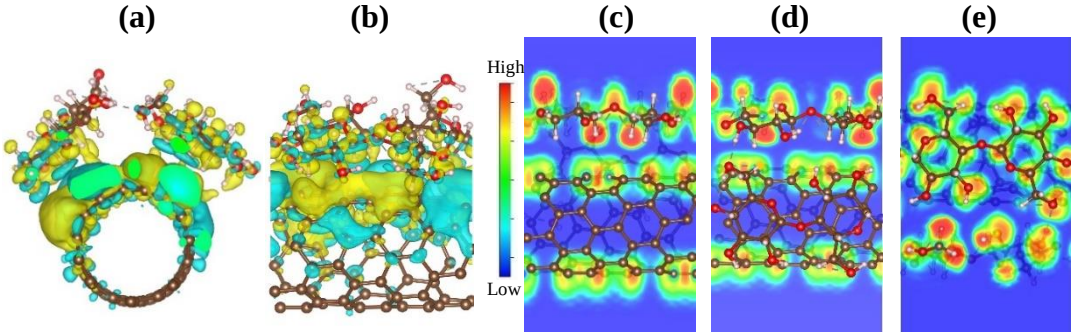

Figure 2. The **(a)-(b)** Charge Density Difference (CDD) and **(c)-(e)** 2D Electron Localization Function (ELF) of the SWCNT/Cellulose nanocomposite. The yellow and cyan isosurface denotes the accumulation and depletion of electronic charge, respectively.

The choice of the prototype SWCNT is due to the close lattice constant between cellobiose and SWCNT(7,1). The equilibrium distance C-C, C-H, and C-O distances of the SWCNT and cellulose are 3.94 Å, 2.88 Å, and 3.83 Å, respectively. The binding energy of a single cellulose chain is -0.608 eV/nm. The adsorption process is exothermic, where the nanocomposite of cellulose chains and SWCNT can form spontaneously and be stable at room

temperature. The calculated binding energy is close to other weakly bonded systems such as the GO/cellulose (-0.9 eV), graphene/polymer (-0.34 eV to -0.76 eV), graphene/nylon-6 (-0.52 eV), and SWCNT/nylon-6 (-0.42 eV) [34–36].

To further examine the synergetic interaction of the nanocomposite, the CDD (Figure 2a and Figure 2b) and ELF (Figure 2c-Figure 2e) are calculated. The Bader charge analysis yields an electron transfer of 0.04 e. The depletion of electronic charge is mainly in the SWCNT (shown in Figure 2a and Figure 2b, tube direction and side view, respectively). It is noted in Figure 2c and Figure 2d that there is no localization of electrons in the interface of the nanocomposite, indicated by the deep blue region. However, deformed ELF is observed particularly at the interface, indicating an induced dipole [37]. In Figure 2e, the cellulose chains interact with one another, showing that the cellulose chains can wrap the SWCNT. This result explains earlier experimental observations that cellulose chains can be utilized to isolate SWCNT [16]. It also supports the claim that cellulose can form tubular structures, as discussed in the following report [38].

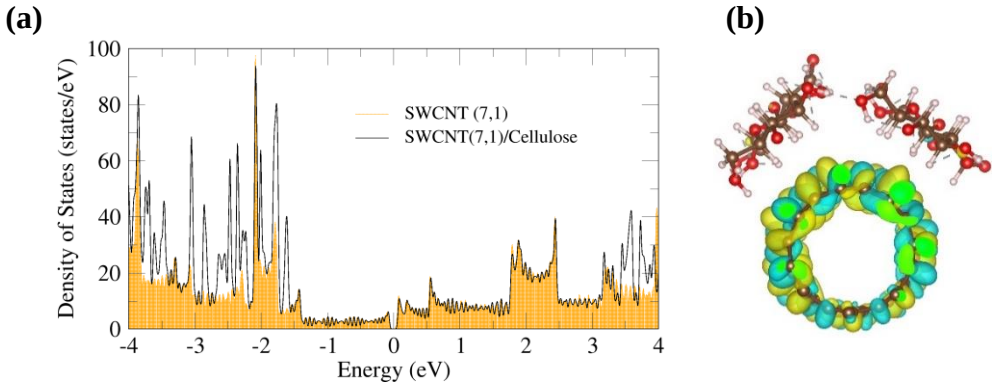

Figure 3. (a) The electronic density of states and **(b)** the charge density of the nanocomposite at the valence band maximum at the Γ point. The Fermi level is taken as the reference (E_{Fermi} = 0 eV).

The electronic density of states of SWCNT(7,1) and the nanocomposite revealed a bandgap of ~0.14 eV (Figure 3a). It is noteworthy to point out that the electronic density of states near the Fermi level (0 eV) is dominated by the SWCNT(7,1), showing that VBM is in the SWCNT(7,1) region (Figure 3b). The electronic states of the cellulose chains appearing at the valence and conduction band are roughly at -1.5 eV and 3.5 eV, maintaining their wide bandgap nature (~ 4.98 eV). The findings indicate that the electronic structure of the SWCNT(7,1) is well maintained where minor broadening of the states is observed, a key feature of physisorption [34, 36]. The results of the density of states of the nanohybrid can be considered a superposition of its constituents with no hybridization of the orbitals between components visible. This result validates the calculated weak binding energy, long-range interaction, minimal charge transfer, and no localization of electrons at the interface of the nanohybrid. The findings confirm that cellulose is suitable for the non-covalent functionalization of carbon nanotubes.

3.2. Cellulose biopolymer for trapping heavy metals.

The optimized configuration of cellulose is shown in Figure 4. As, Hg, and Pb adsorption are investigated in four adsorption sites shown in Figure 4b. The calculated binding energy, minimum distance, and bandgap are summarized in Table 1.

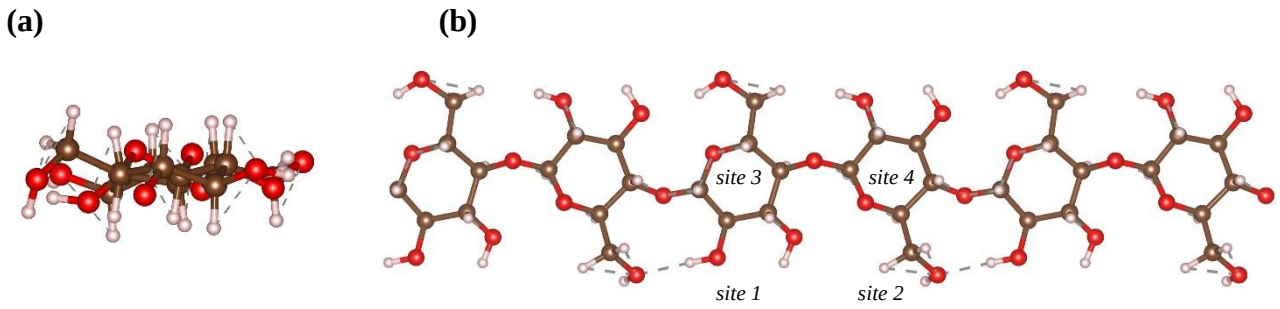

Figure 4. The optimized cellulose chain is viewed from the **(a)** chain direction and **(b)** top view.

The optimized configuration of cellulose with adsorbed As, Hg, and Pb are displayed in Figures 5a, 5b, and 5c, respectively. For the Cellulose-As and Cellulose-Pb configurations, the adsorption energy is maximum in site 1, where the hydroxyl group of cellulose interacts with As and Pb with a bond length of 2.06 Å and 2.50 Å, and corresponding binding energy of -1.05 eV and -0.58 eV, respectively. The bonding is mainly due to the hydroxyl-As and hydroxyl-Pb interactions. On the other hand, a relatively weaker interaction is observed between cellulose and Hg in all sites. However, the magnitude of the binding energy is still higher than the thermal energy (25 meV), indicating that Hg can be trapped at room temperature but can quickly diffuse in the system. In site 3, the As, Hg, and Pb are physisorbed as reflected by the equilibrium distances showing no formation of a bond between the heavy metals and cellulose. In site 4, the As and Pb formed a bond with the oxygen atom of the cellulose, but the binding energy is lesser compared to site 1. These results agree with and confirm other reports that cellulose and other natural polymers are suitable as adsorbent materials for heavy metals [12, 39–41].

Table 1. Summary of the binding energy, minimum distance, and bandgap of cellulose chain and heavy metals (As, Hg, and Pb) systems displayed in Fig.5. The bandgap of cellulose is 4.98 eV.

System	Min. Distance {Å}	Binding Energy {eV}	Bandgap {eV}
Cellulose – As			
Site – 1	2.06	-1.05	1.63
Site – 2	2.07	-0.77	1.41
Site – 3	1.89	-0.35	2.61
Site – 4	2.12	-0.66	1.37
Cellulose – Hg			
Site – 1	2.73	-0.13	4.70
Site – 2	3.21	-0.09	4.64
Site – 3	2.98	-0.16	4.83
Site – 4	3.35	-0.17	4.89
Cellulose – Pb			
Site – 1	2.50	-0.58	0.09
Site – 2	2.64	-0.26	0.03
Site – 3	3.08	-0.20	2.67
Site – 4	2.67	-0.41	0.94

The charge density isosurface of cellulose with adsorbed As, Hg, and Pb are further investigated in Figure 6. At the isosurface value of 0.035, overlapped electrons are shown in Figure 6a and Figure 6d between cellulose and As, indicating sharing of electronic charge. The cellulose and Pb systems show overlaps of electronic density in Figure 6c (at the OH-Pb region). However, no sharing of electronic charge at site 3 (Figure 6f), justifying its calculated weak binding energy. In both cases of cellulose-Hg systems (Figure 6b and Figure 6e), no overlapping electronic charge is observed, explaining the weak interaction of Hg.

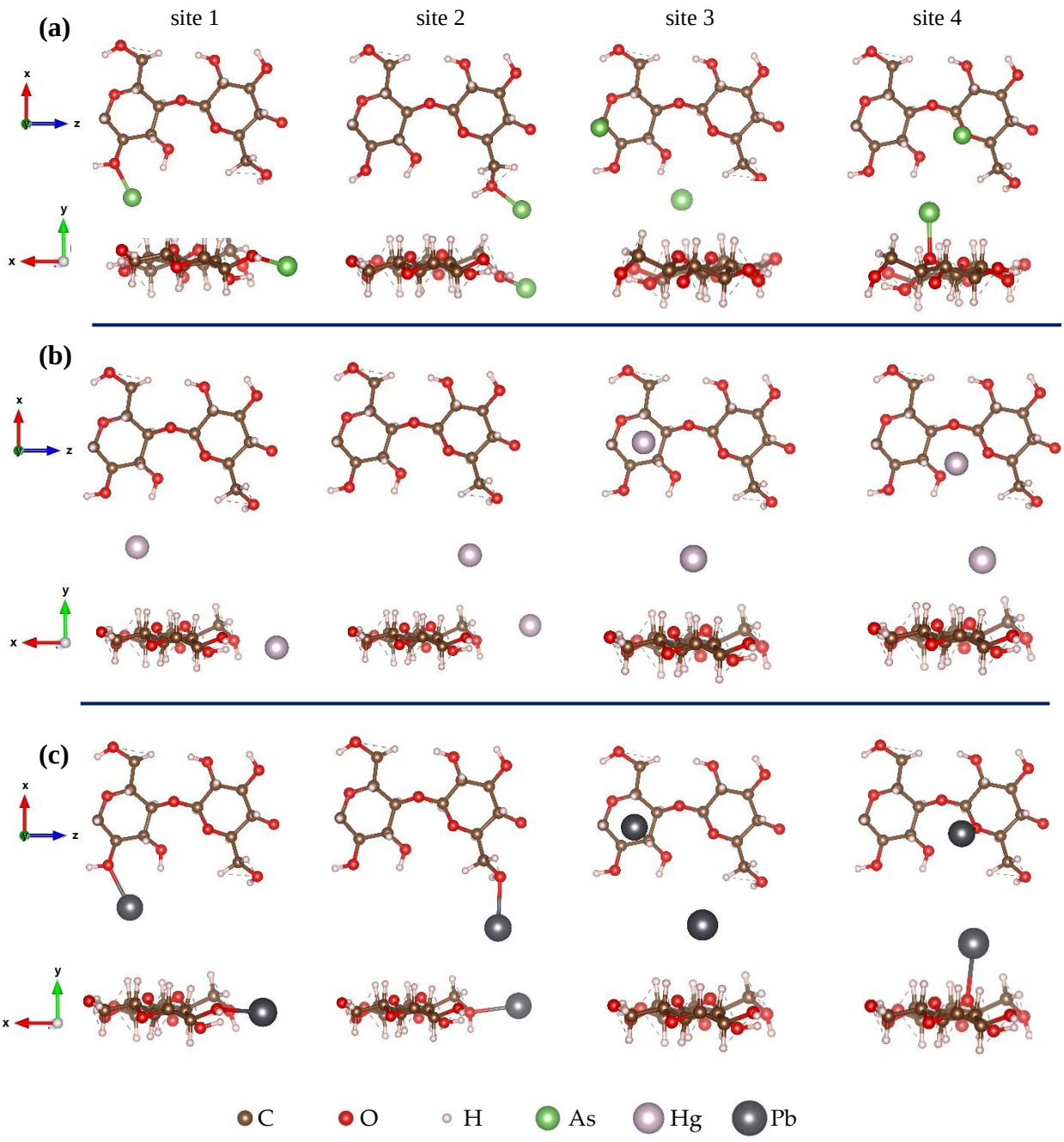

Figure 5. The optimized structure of **(a)** Cellulose-As, **(b)** Cellulose-Hg, and **(c)**Cellulose-Pb systems in four sites.

The calculated bandgap of the cellulose is 4.98 eV, which agrees with a recent report (5.0 eV–5.5 eV) [42]. Significant bandgap reduction is observed in Cellulose-As and Cellulose–Pb systems, while Cellulose–Hg systems maintain the wide bandgap nature of cellulose. The electronic bandgap is related to the material's conductivity and absorption spectra, in which significant changes in the material's bandgap can be utilized as sensing criteria [43]. Thus, based on these findings, cellulose can be used for trapping and sensing heavy metals such as As and Pb.

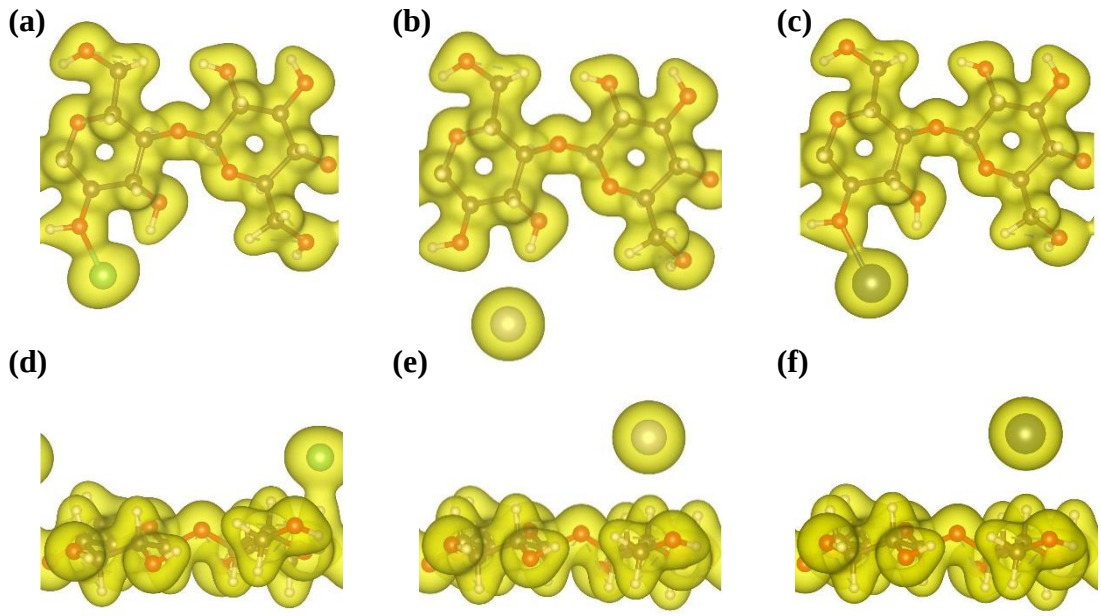

Figure 6. The charge density of cellulose with adsorbed As, Hg, and Pb in **(a)-(c)** site 1 and **(d)-(f)** site 3. The charge density isosurface value is set to 0.035.

Further calculations are still needed to reveal the interaction of heavy metals and their compounds to fully elucidate the potential of cellulose as an adsorbent and sensing material for heavy metals. The topological analysis of electrons is also essential to further understand the interaction of cellulose and heavy metal systems. Moreover, higher-level theory and hybrid exchange-correlation functionals can be ideally used to examine the excited properties of cellulose and heavy metals systems. Although DFT under PBE level theory is known to underestimate the band gap of semiconductors and insulators, the results can provide important and valuable trends of the many-body electronic system, which helps understand the properties of materials at the fundamental level [34, 39, 41, 44–47].

4. Conclusions

First-principles density functional theory calculations are conducted to explore the applicability of cellulose as a functional dispersant of SWCNT and adsorbent material for trapping heavy metals. The findings show that cellulose is physisorbed on the SWCNT. This claim is based on the calculated weak binding energy, no value of ELF in the interface, and no hybridization of the orbital characters observed between cellulose and SWCNT. The optimized configuration of the nanocomposite revealed a long-range interaction of cellulose and SWCNT. Further calculations show that cellulose is suitable for trapping heavy metals such as As and Pb, while a relatively weaker interaction is observed in Hg. To conclude, first-principles calculations show cellulose has diverse technological applicability, such as a functional dispersant material for SWCNT and adsorbent–sensing material for heavy metals.

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Conflicts of Interest

The authors declare no conflict of interest.

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