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Functionalization of single-walled carbon nanotubes with uracil, guanine, thymine and L-alanine

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ABSTRACT

Experimental investigation of functionalization of oxidized single-walled carbon nanotubes (OSWCNTs) with three nucleic acid bases such as uracil, guanine, thymine and one amino acid, L-alanine is carried out. Initially, the SWCNTs are oxidized by acid treatment. Further, the oxidized SWCNTs are effectively functionalized with aforementioned biological compounds by ultrasonication. The diameter of OSWCNTs has increased after the adsorption of biological compounds. The cumulative Π–Π stacking, hydrogen bond and polar interaction are the key factors to realize the adsorption. The amount of adsorption of each biological compound is estimated. The adsorption of guanine is more among all the four biological compounds.

1. Introduction

Nanomaterials are the materials having dimension in the nanometer regime comparable to many biological molecules such as enzymes, antibodies, nucleic acids and so on that are present in the living systems. Materials in the nanoscale regime display interesting properties distinct from their bulk nature thereby opening new opportunities for biological research and applications. Carbon nanotubes (CNTs), the cylindrically rolled graphene sheets exhibits unique physical, chemical and mechanical properties such that they have gained more attention among the research community [1–3]. Applications of CNTs and CNTs based materials have covered the area such as electronics [2,3], hydrogen storage [4,5] and so on. In recent years, efforts have been put forward to explore the potential biological applications of CNTs [6,7]. The process of functionalization of CNTs by different methods can overcome the obstacles such as dispersion and separation associated with CNTs upon their usage [8–13]. The investigations of functionalization of CNTs with biological molecules could lead to possible applications of CNTs such as gene therapy, drug delivery, bio-sensing and so forth.

Extensive investigations have been carried out on functionalization of CNTs with biological molecules like proteins, amino acids and DNA [10–13] to understand the interaction between them. Zheng et al. [8,9] have utilized DNA to disperse and separate the CNTs. The functionalization of SWCNTs with cytosine and guanine using ab-initio calculations has displayed self-assembling character and formation of a ladder configuration [14]. Das et al. [15] have reported the binding energy of various nucleobases (guanine, adenine, thymine and cytosine) with (5, 5) SWCNT using first-principle calculations. The activation enthalpies for the binding of nucleobases on CNTs have been measured [16]. Singh et al. [17] have reported the formation of self-assembled nanorings as a result of functionalization of SWCNTs with uracil nucleobase. On the other hand, proteins are large biological molecules consisting of one or more amino acids arranged in a linear chain connected together by peptide bonds. It is obvious that the binding of protein with CNT is influenced by individual amino acids present in the protein [18–20]. The non-covalent and covalent approaches have been used for the functionalization of CNTs with amino acids [21,22]. The increase in solubility of CNTs in polar solvents has been achieved with the amino-functionalized fluorinated CNTs [23]. Recently, Piao et al. [24] have investigated the interactions between oxidized SWCNTs (OSWCNTs) and three amino acids such as L-glycine, L-lysine and L-phenylalanine. The amino acids that are adsorbed on OSWCNTs have formed a stable suspension in water medium.

In this direction, we have carried out the experimental investigation of functionalization of OSWCNTs with nucleobases such as uracil, guanine, thymine and an amino acid L-alanine. All these four biological compounds are encoded by genetic information. We have chosen one RNA base-uracil (U), one DNA base-thymine (T) and guanine (G)-a base present in both RNA and DNA and one amino acid-Alanine (A) for the investigation. Alanine is simplest and smallest amino acid and we have considered L-alanine for the investigation. Previously, our theoretical research group has

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carried out the DFT simulation studies on interaction between the aforementioned biological compounds and SWCNTs [25–29]. These studies have indicated that the binding of nucleobases and amino acid on SWCNT surface is feasible and the resultant structure is stable through functionalization. The present experimental work is a follow up of our theoretical investigations.

2. Experimental

The SWCNTs are purified and shortened by suspending the as-received CNTs in a solution containing concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3) mixed in a ratio of 3:1 by volume, respectively. This solution is then ultrasonicated vigorously in water bath for 12 h at room temperature. The resultant suspension is then diluted by washing with deionized water and dried in a vacuum oven for a day at room temperature. As a result, the ends and sidewalls of CNTs bear oxidized carbon sites such as carboxylic acids and the resultant SWCNTs is named as OSWCNTs. A schematic illustration of SWCNT and OSWCNT is presented in the Supplementary information as Figure S1.

In a typical functionalization experiment, 20 mg of OSWCNTs are mixed with 100 mg of the biological compound in 50 ml water medium. The solution is then ultrasonicated in water bath for 3 h at room temperature. The solution that has resulted from ultrasonication is centrifuged for 30 min, filtered and dried in a vacuum oven for a day at room temperature. The functionalized samples are labeled as C-U, C-T, C-G and C-A to denote the CNTs-uracil, CNTs-thymine, CNTs-guanine and CNTs-alanine respectively.

3. Results and discussion

Figure 1a–e shows the TEM images of OSWCNTs samples before (Figure 1a) and after functionalization with uracil (Figure 1b), guanine (Figure 1c), thymine (Figure 1d) and L-alanine (Figure 1e). The Figure 1a displays the well separated and clean sidewalls of OSWCNTs before functionalization. From Figure 1b–e, one can observe the coverage of biological compounds on the sidewall of OSWCNTs in comparison with the Figure 1a. Inset in Figure 1b–e show zoomed images of the corresponding functionalized samples. Figure 1f–j shows the corresponding ED spectra of all the samples. It is confirmed that the elemental nitrogen is existed in the functionalized samples (Figure 1g–j). In contrast, there is no elemental nitrogen in OSWCNTs before functionalization. This indicates that, the biological compounds are adsorbed on OSWCNTs after functionalization. It is also noted in all spectra that, the presence of metal catalyst, Ni (that might be used during the synthesis of SWCNTs) along with Cu peak resulted from the grid during analysis.

Raman spectroscopy is the most sensitive tool to characterize carbon nanostructures [30,31]. Figure 2 shows radial breathing modes (RBM) in the Raman spectra of OSWCNT samples before (Figure 2a) and after functionalization with uracil (Figure 2b), guanine (Figure 2c), thymine (Figure 2d) and L-alanine (Figure 2e). Generally, bands in the range of 100–300 cm^{-1} are attributed to RBM of SWCNTs. The RBM is being used to determine the diameter of SWCNTs through its frequency [30,31]. In Figure 2, one can observe the two RB modes in the specified region. The diameters of OSWCNTs are 0.950 and 1.548 nm for the corresponding RB modes at 251 and 154 cm^{-1}, respectively before functionalization (Figure 2a). From Figure 2, it is clear that the larger diameter OSWCNTs (154 cm^{-1}) has been significantly affected by functionalization. The RBM at 154 cm^{-1} of OSWCNTs shows a remarkable downshift in frequency (8 cm^{-1}) after functionalization. On the other hand, the RBM at 251 cm^{-1} displays a downshift of 5 cm^{-1} after functionalization. The downshift in frequency indicates the increase in diameter of OSWCNTs with the adsorption of biological compounds. Piao et al. [24] and Liu et al. [32] have shown that the RBM of SWCNTs has a downshift when molecules were adsorbed on SWCNTs. The results in the current study suggest that the biological compounds are adsorbed on the external wall of OSWCNT and the adsorption layer thickness of guanine on OSWCNT is thicker than that of other compounds. This is confirmed by the increase in diameter of OSWCNTs after functionalization. The band intensity at 251 cm^{-1} of OSWCNTs has a remarkable decline in intensity when compared to the intensity of band at 154 cm^{-1} of OSWCNTs after the adsorption of biological compounds. This means that the smaller diameter tubes are affected more due to its curvature effect than the larger diameter tube [33,34]. Hence, smaller the diameter of OSWCNTs, higher is the chemical reactivity and adsorption of the biological compounds. The Π–Π stacking interaction between SWCNTs and biological compounds induced a shift in the frequency of RBM [24,25]. In addition, our simulation studies have indicated the existence of Π–Π stacking interaction between SWCNTs and biological compounds [25–27]. From the above results, the adsorption amount of guanine on OSWCNTs is likely to be more among all the four biological compounds. The reason may be the formation of more intermolecular hydrogen bond between the guanine species because each guanine comprises three amino groups. Generally, the intermolecular hydrogen bond is formed when the biological molecule contains (more than one) amino group [24]. A recent DFT study of interaction between nucleobases and graphene oxide (GO) flakes also shows the strong binding of guanine on GO flakes [35].

In the high frequency region of 1300–1600 cm^{-1}, there are two modes associated with SWCNTs. The disordered (D) and graphitic (G) bands are the two characteristic bands for SWCNTs. Usually, the D band appears in the range of 1300–1400 cm^{-1}, and it is attributed to the disorder in CNTs. The most intensive tangential (G) mode is the high energy mode of SWCNTs, which normally exists in the range of 1565–1595 cm^{-1}. The G band arises from in-plane tangential stretching of C—C bonds in CNTs which has appeared due to the vibration of carbon atoms along the nanotube axis. The G band of SWCNTs denotes the cylindrical symmetry perfection of CNTs. The cylindrical symmetry of SWCNTs will be affected by the adsorption of chemical species. So, the adsorption of biological compounds on SWCNTs would be resulted in the occurrence of change in the G band. Previous reports [34,36] have showed that the G mode is sensitive for the charge transfer from doped species to CNTs. Moreover, the upshift in G band is the resultant of electron removal from SWCNTs [36,37]. The results of the present study are in agreement with earlier reports [34,36,37]. From Figure 3, it is observed that the G band has upshifted from 1582 cm^{-1} to 1587, 1588, 1587 and 1586 cm^{-1} due to the adsorption of uracil, guanine, thymine and L-alanine, respectively. In addition, the shape of the G band has got disturbed. It means that, the biological compounds are electron acceptors during the interaction process. The upshift of the G band after functionalization is associated with the formation of a polar interaction between the biological compounds and sidewalls of OSWCNTs. On the other hand, the increase in intensity of D/G ratio is a measure that resulted from the adsorption of chemical species on SWCNTs and higher the D/G intensity ratio the higher the adsorption [38,39]. The D/G intensity ratio of all the samples is denoted in Figure 3. As the D/G intensity ratio of the guanine adsorbed OSWCNTs shows the higher value of 0.270 than other compounds, it has more adsorption on OSWCNTs. This observation agrees with the result of RBM analysis of Raman spectra.

IR analysis is being used effectively for the study of functional groups attached to SWCNTs. Figure 4a–c shows the IR spectra of OSWCNTs, uracil and OSWCNTs functionalized with uracil, respectively. The IR spectrum of OSWCNTs displays a peak at 1634 cm^{-1},