Simulation of graphene–fullerene nanohybrid structure

J MEENA DEVI

Centre for Nanotechnology and Advanced Biomaterials (CeNTAB), School of Electrical and Electronics Engineering (SEEE), SASTRA Deemed University, Thanjavur 613401, India
jmeenadevi@sastra.ac.in

MS received 4 May 2018; accepted 31 August 2018; published online 7 March 2019

Abstract. In the present simulation study, the structure and dynamics of graphene–fullerene nanocomposite has been investigated using all atom molecular dynamics simulation technique. The formation of graphene–fullerene nanocomposite constituting graphene and self-assembly of 12 bucky balls has been demonstrated. The structure, size, interparticle separation, spatial distribution, temperature effect, mobility and conformation of graphene–fullerene nanocomposite, and the influence of single and two layers of graphene on the structure of graphene–fullerene nanocomposite have been determined and discussed in detail. This simulation result may possibly aid the design and development of graphene–fullerene hybrid nanomaterials for future biological and technological applications.

Keywords. Graphene; fullerene; nanohybrid; self-assembly; molecular dynamics simulation.

1. Introduction

The nanostructured carbon allotropes such as graphene and fullerene have extraordinary and fascinating physicochemical properties owing to their unique bonding, and band structure. Graphene is an atomically thin two-dimensional (2D) hexagonal honey comb lattice of sp^2 -hybridized carbon atoms. It is a zero-gap semi-metal with a direct Fermi Dirac band structure. It has many remarkable properties such as high surface area, electrical conductivity, carrier mobility, thermal conductivity, Young's modulus, optical transparency, the thinnest barrier and excellent chemical stability [1–4]. Graphene is functionalized to tailor the properties of graphene for the desired applications. Graphene and graphene derivatives have been demonstrated to have potential applications in a wide range of areas such as biomedical science, sensors, batteries, supercapacitors, solar cells, fuel cells, display screens, spintronic devices, field-effect devices, nano-electronics, smart textiles, toxic material removal, water remediation, drug delivery and biotechnology [3–10].

Fullerene (C_{60}) is a symmetric, three-dimensional (3D), hollow, spherical closed-cage molecule, resembling the geometry of the truncated icosahedron and soccer ball. Buckminster fullerene consists of 60 carbon atoms located at the vertices of 12 pentagons and 20 hexagons. Fullerene is a semiconductor and it can be converted into conductor or superconductor by doping with alkali metals. It possesses high electron affinity, bulk modulus, permeability through biological barriers, good bio-compatibility, unique photo-optical property, excellent stability, antiviral activity, antioxidant activity, radical scavenging ability and cytotoxicity [11–15]. It can entrap metal atoms, ions or small molecules inside

the carbon cage [16]. Fullerene and its derivatives are applicable in divergent areas such as photo-voltaic devices, fuel cells, nano-memory device, optical device, sensors, antioxidant drugs, catalysis, magnetic resonance imaging, photo dynamic therapy, targeted drug delivery system, skin treatment, biomedicine and bioengineering [14–22].

Nanohybrid structures involving graphene and fullerene have generated scientific interest due to the enhanced and new synergistic properties and function. Graphene–fullerene-based nanocomposite holds great promise for potential applications in different fields such as nano-electronics, optoelectronics, lasers, nano-mechanics, energy storage, energy conversion, spintronics, catalysis, sensors, cancer therapy and medical biology [23–30]. In the literature some molecular dynamics (MD) and density functional theory (DFT) based simulation studies on the interactions between graphene and fullerene and 2D materials have been reported [31–46].

DFT calculations have been performed to study the charge transfer, electronic, magnetic and structural characteristics of various graphene–fullerene nanohybrid structures in the literature [41–46]. In the literature [31–40], MD simulation technique has been employed to study the motion of single fullerene on graphene sheet; structure of sandwiched fullerene molecules between layers of graphene; self-assembly of fullerene over graphene/carbon-based 2D materials; construction of nanoporous graphene with fullerene; molecular self-assembly over black phosphorene. Mukhopadhyay *et al* [40] have reported the minimum cytotoxicity of novel bio-compatible 2D material based on carbon (C_2N) from their MD simulation studies.

Xu *et al* [36] have reported the formation of a scroll peapod structure produced by spontaneous scrolling of

graphene nanoribbon (stabilized with the hydrogen atoms along the edges) onto a fullerene string of two to five C_{180} fullerene molecules by using MD simulations. Feng *et al* [37] have studied the self-assembly of graphene nano-ribbon (stabilized with the hydrogen atoms along the edges) and fullerene molecules of different sizes such as C_{60} , C_{180} , C_{240} , C_{320} and C_{540} by using MD simulations. They have reported the influence of width of graphene nanoribbon, size and number of fullerene molecules on the structure of resulting self-assembly. Osmaian *et al* [38] have carried out MD simulation studies to investigate the self-assembly of 100 C_{60} fullerene molecules, initially located on a simple cubic lattice above the graphyne sheet (allotrope of carbon consisting of carbon–carbon acetylenic bonds and benzene rings with different ratios). They have identified the influence of the different types (different number of carbon–carbon triple bonds) of graphyne on the mobility and morphology of self-assembly of fullerene molecules.

In the present work, MD simulations are performed to investigate the structure and dynamics of two types of graphene fullerene nanocomposites in which one involves the combination of single pristine graphene layer and 12 fullerene C_{60} molecules and the other one involves the combination of two pristine graphene layers and 12 fullerene molecules. This simulation study may throw some light about the self-assembly of the fullerene molecules on the surface of graphene and the influence of number of graphene layers on the structure of the graphene–fullerene nanocomposite.

The MD simulation studies on the graphene–fullerene nanocomposite will enrich the understanding of their structure and dynamics at the atomic level. In the present study, graphene–fullerene nano-hybrid structures are simulated at three different temperatures 200, 300 and 400 K to investigate their structural features. The nanocomposite constituting a combination of graphene and fullerene will be of great benefit and advantage due to their biocompatibility, unique optical, electrical, thermal, mechanical, catalytic, chemical and bio-chemical properties and they have potential applications in nanotechnology. The results of this computational work may possibly aid the design and development of the graphene–fullerene nanocomposite as a component for nanoscale devices and biological applications.

2. Materials and methods

Two systems of graphene–fullerene nanohybrid structure namely Single-gb and Double-gb were studied and the details of these two systems are given in table 1. The initial configuration of the Single-gb system consists of 12 bucky balls (C_{60}) on the top of a single monolayer graphene sheet while the initial configuration of the Double-gb system consists of 12 bucky balls (C_{60}) in-between the two monolayer graphene sheets as shown in figure 1. The dimension of the graphene sheet is around 160×139 Å. Each sheet of graphene contains 8712 number of carbon atoms. The distance between

Table 1. Constituents of graphene–fullerene nanocomposite.

Sl. no.	System	No. of graphene sheets	No. of bucky balls
1	Single-gb	1	12
2	Double-gb	2	12

Figure 1. Initial configuration of graphene–fullerene nanohybrid structure. Graphene carbon atoms (blue) are shown in Licorice representation and fullerene carbon atoms (pink) are shown in van der Waals representation.

the bottom graphene sheet and bucky balls is around 5 Å. The interparticle separation between two bucky balls is around 21 Å (centre of mass distance between the two nearest bucky balls).

The force field parameters for the graphene and fullerene carbon atoms were taken from the aromatic carbon atoms of the CHARMM27 force field [47]. In the literature, the CHARMM27 force field parameters [48–52] have been reported to yield significant results for the graphene and fullerene systems. Sathe *et al* [48] have used the CHARMM27 force field parameters for graphene to study the detection of DNA by graphene nanopores. Luo *et al* [49] have employed the CHARMM27 force field parameters for the polyethylene glycol-functionalized graphene oxide nanosheets to investigate their interactions with the cell membrane. Saikia *et al* [50] have applied CHARMM27 force field parameters for graphene to describe the self-assembly of cytosine bases on graphene. Kraszewski *et al* [51] have modelled functionalized fullerene using the CHARMM27 force field parameters to study their interactions with the model cell membrane. Kraszewski *et al* [52] have used CHARMM27 force field parameters for the fullerene molecules to study their interactions with the potassium channels. So the approach of modelling the graphene and fullerene carbon atoms using CHARMM27 force field parameters can yield correct description for the present study on structure and dynamics of the graphene–fullerene nanocomposite.

In the present work, all the MD simulations have been carried out using the NAMD [53] package under NVT ensemble at three different temperatures 200, 300 and 400 K. Langevin dynamics has been used with a damping coefficient of 5 ps^{-1} for temperature control. Periodic boundary conditions were

Figure 2. Snapshots of graphene–fullerene nanocomposite at the end of the simulation (300 K).

imposed. Energy minimizations were performed using the conjugate gradient energy minimization method and the number of steps taken for minimization was 3000. A time step of 2 fs was used for integrating equations of motion and the two systems were run for 30 ns. All the analyses were done for the last 10 ns.

3. Results and discussion

MD simulations have been carried out to study the two graphene–fullerene nanohybrid systems namely Single-gb and Double-gb under NVT ensemble at three different temperatures 200, 300 and 400 K for a period of 30 ns. The final configurations of the graphene–fullerene nanocomposite obtained from the MD simulation at room temperature are presented in figure 2. The self-assembly of the bucky balls and graphene has resulted in the formation of a graphene–fullerene nanocomposite. The stronger intermolecular interactions between graphene and fullerene have brought them together to form a nanocomposite.

In the case of the Single-gb system, three aggregates of bucky balls are formed on the graphene sheet. Among the three aggregates, one is larger (BA1) in size composed of eight bucky balls arranged in two rows and the other two aggregates are smaller (SA1 and SA2) in size with just two bucky balls. In the case of the Double-gb system, a single aggregate of bucky balls is formed on the graphene sheet. During the process of self-assembly in Double-gb system, top and bottom graphene sheets have stacked together and an aggregate of bucky balls lie above the two stacked graphene sheets. The inter-sheet interactions have stacked the two graphene sheets together. The structure of the graphene–fullerene nanocomposite obtained from the present simulation study is a layered structure with the layers of graphene and fullerene and it is consistent with some results reported in

Figure 3. Relative interaction energy between graphene and fullerene (300 K).

the literature. Mirzayev *et al* [35] have observed the structure of the graphene–fullerene nanocomposite in a sandwich form both through their experimental as well as simulation studies. Verhagen *et al* [54] have reported the preparation of graphene–fullerene nanocomposites in a sandwich form by chemical vapour deposition method.

3.1 Energy estimation

The relative interaction energy between graphene and fullerene for the two systems Single-gb and Double-gb at room temperature are given in figure 3. The relative interaction energy is obtained by subtracting the interaction energy from minimum interaction energy. In the case of the Single-gb system, there is not much variation in the interaction energy within the simulated time. In the case of the Double-gb system, there is a sudden drop in the energy around 0.8 ns and after 4 ns energy fluctuations have become minimum and uniform. The sudden drop in the energy at 0.8 ns corresponds to the stronger interactions between the two graphene sheets which pulls them together from their initial (centre of mass distance) spacing of around 22.3 Å to a stable spacing of 3.8 Å. In the initial configuration, 12 bucky balls are placed in the region between the two graphene sheets. With the evolution of time, two graphene sheets stack together, while the bucky balls aggregate on the top of the stacked graphene sheets. The two graphene sheets have stacked together due to the π – π interactions between them. Then the bucky balls have got deposited on the surface of the stacked graphene sheets due to the non-bonded interactions between graphene and fullerene.

The binding energy (BE) of the graphene–fullerene nanohybrid structure can be calculated by subtracting the energy of the individual components from the energy of the system

Figure 4. Time evolution of radius of gyration of graphene–fullerene nanocomposite (300 K).

in the nanocomposite form:

$$BE = E_{NC} - (E_{m\text{-graphene}} + E_{n\text{-fullerene}}). \quad (1)$$

In the above equation, E represents total energy, NC represents nanocomposite; m represents the number of graphene sheets and n represents the number of fullerene balls. The BE values estimated using equation (1) for the Single-gb and Double-gb systems are -258.21 and -281.65 kcal mol $^{-1}$ respectively. The BE is more negative for the Double-gb system, since there will be π – π interactions between the two graphene sheets along with the interactions between graphene and fullerene. Hence the Double-gb system is more stronger and stable.

3.2 Size and spatial distribution

The exact numerical values of the size of the graphene–fullerene nanocomposite are essential for designing nanoscale devices and for incorporating the nanocomposite inside the biomolecules for biological and sensing applications. The size of the graphene–fullerene nanocomposite at room temperature is determined from the calculation of radius of gyration and the time evolution of radius of gyration of the graphene–fullerene nanocomposite is shown in figure 4. The average size of the graphene–fullerene nanocomposite calculated for the last 10 ns for the two systems Single-gb and Double-gb

Figure 5. Time evolution of COM distance between graphene and bucky balls (300 K).

are 60.35 ± 0.15 and 61.21 ± 0.11 Å, respectively and they are shown in table 2. The double layer graphene–fullerene nanocomposite is more compact and dense due to the formation of a single aggregate of bucky balls and stacking of two graphene sheets together.

The movement of the fullerene molecules (12 bucky balls) with respect to graphene can be identified from the centre of mass distance between them and it is shown as a function of time in figure 5. The average centre of mass (COM) distance between the fullerene molecules and graphene at room temperature for Single-gb and Double-gb systems calculated for the last 10 ns is 25.04 ± 3.22 and 48.80 ± 3.64 Å, respectively and they are given in table 2. There is around 12.8% fluctuation in the average COM distance between fullerene and graphene in the case of Single-gb system and 7.4% fluctuation in the case of Double-gb system. This illustrates the smooth, continuous and collective motion of fullerene with respect to graphene. The fluctuation is relatively less in the two layer graphene. This may be due to the stronger binding between graphene and fullerene originating from the presence of two layers of graphene. Neek-Ammal *et al* [31] have reported the diffusive motion of fullerene molecule over monolayer graphene from their MD simulation work. Savin *et al* [33] have studied the motion of fullerene on graphene nano-ribbon under the influence of electric field and heat gradient employing MD simulation technique.

The distance between the two graphene sheets and their movement in the Double-gb system at room temperature can

Table 2. Structural details of graphene–fullerene nanocomposite (300 K).

Sl. no.	System	Size of graphene–fullerene nanocomposite (Å)	COM distance between graphene and fullerene (Å)
1	Single-gb	60.35 ± 0.12	25.04 ± 3.22
2	Double-gb	61.21 ± 0.11	48.80 ± 3.64

Figure 6. Time evolution of centre of mass between graphene sheets (Double-gb) (300 K).

Figure 7. Radial distribution function between graphene carbon atoms and fullerene carbon atoms (300 K).

be estimated from the COM distance between them and it is shown in figure 6. The average COM distance between the two graphene sheets is 3.82 ± 0.02 Å. The tiny fluctuations in the average COM distance between the graphene sheets indicate their stable aggregation and lower mobility. Guan *et al* [27] have estimated the interlayer spacing of graphene–fullerene hybrid structure to be 3.7 Å from their high-resolution transmission electron microscopy measurements.

The distance and distribution of the graphene carbon atoms and fullerene carbon atoms within the graphene–fullerene nanocomposite at room temperature can be quantified from the radial distribution function between them (figure 7). The most probable distance between the graphene and fullerene carbon atoms is 9.85 Å. Neek-Ammal *et al* [31] have reported the centre of mass distance between single fullerene molecule and graphene sheet to be 6.50 Å along the z axis. The radius of a fullerene molecule is around 3.5 Å. So the present computed most probable distance between graphene and fullerene lies in the range of value reported by Neek-Ammal *et al* [31].

Figure 8. Variation of RMSD values of graphene and fullerene carbon atoms with time (300 K).

3.3 Mobility

The estimation of the root mean square deviation (RMSD) values of the bucky balls may be helpful in their industrial and biomedical applications. The time variation of the RMSD values of the bucky balls and graphene at room temperature are shown in figure 8 and their average values are shown in table 3. The RMSD values of the bucky balls of the Single-gb and Double-gb systems are 11.99 ± 2.66 and 4.93 ± 0.32 Å, respectively. Saikia *et al* [55] have estimated the RMSD value of a bucky ball to be around 11 Å from their MD simulation study on the release of drug molecules from carbon nanotube mediated by fullerene. The RMSD value of the bucky balls of Single-gb system lies in the range of the RMSD value estimated by Saikia *et al* [55].

In the Single-gb and Double-gb systems, RMSD value of the fullerene carbon atoms is larger than the RMSD value of graphene carbon atoms. So the bucky balls have higher mobility than the graphene sheets. This may be due to the smaller size, lower mass and the 3D soccer ball shape of bucky balls which might have facilitated their movement. The 2D structure, relatively larger size and heavier mass of the graphene sheets might have hindered their movement.

When we compare the RMSD values of graphene of the two systems Single-gb and Double-gb, mobility of graphene of the single layer is 1.6 times larger than the double layer. The presence of two layers of graphene sheets and interactions between them might have hindered their free movement to some extent. The mobility of the bucky balls of the single layer is 2.4 times larger than the double layer. This difference may be attributed to formation of three aggregates and relatively lesser binding between graphene and fullerene. As noted earlier, the fluctuations in COM distance between graphene and fullerene molecules (figure 5) were larger for the Single-gb system. The same trend is again reflected in the RMSD values. So the mobility of the single-layer graphene–fullerene nanocomposite is larger. Hence the mobility of bucky balls in

Table 3. RMSD values of graphene and fullerene carbon atoms (300 K).

Sl. no.	System	Graphene carbon atoms (Å)	Fullerene carbon atoms (Å)
1	Single-gb	1.47 ± 0.40	11.99 ± 2.66
2	Double-gb	0.91 ± 0.16	4.93 ± 0.32

Figure 9. Time evolution of radius of gyration of aggregate of bucky balls (300 K).

the graphene–fullerene nanocomposite may be modified by varying the number of graphene layers. Osmaian *et al* [38] have evaluated the mobility of the fullerene molecules on graphyne sheets from the mean square deviation values. They have reported that the decrease in the mobility of fullerene with the increase in the number of carbon–carbon triple bonds in the graphyne sheets.

3.4 Self-assembly of fullerene

The size and structure of aggregate of the bucky balls on graphene is important for their sensing and technological applications. The self-assembly of bucky balls on the surface of the graphene is found to be different for the two systems. As mentioned earlier, the single layer graphene–fullerene nanocomposite has three aggregates of the bucky balls (BA1, SA1 and SA2), while single layer graphene–fullerene nanocomposite has one large aggregate of the bucky balls at room temperature. The size of the aggregate of the bucky balls is determined from the calculation of radius of gyration. The time evolution of radius of gyration of aggregate of the bucky balls is shown in figure 9. The average size of the aggregates calculated for the last 10 ns at room temperature for the two systems is shown in table 4. From figure 9 we can also infer the time of formation of the aggregate. An aggregate of the bucky balls of two layer graphene has formed earlier at 2 ns and it is compact and the fluctuation in its size

Table 4. Self-assembly of fullerene (300 K).

Sl. no.	System	No. of aggregates	Size of aggregate (Å)
1	Single-gb	3	
		BA1	18.97 ± 1.72
		SA1	6.13 ± 0.08
2	Double-gb	SA2	6.14 ± 0.08
		1	12.11 ± 0.05

is very less. The time of formation of three aggregates is different in the case of the single layer of graphene.

The spacing between the bucky balls within the aggregate can be obtained from the centre of mass distance distribution shown in figure 10. The uniform, ordered spatial distribution of bucky balls is evident from the presence of evenly placed multiple narrow peaks in figure 10. The most probable COM distance between the bucky balls is 9.5 Å. During the process of self-assembly of fullerene, bucky balls have come closer towards a distance of 9.5 Å from the initial interparticle distance of 21 Å. Mirzayev *et al* [35] have reported the distance between the centres of neighbouring fullerene molecules in the graphene–fullerene nanocomposite to be 9.60 Å. Hence the spacing between the bucky balls determined from the present work closely resembles the values reported by Mirzayev *et al* [35].

3.5 Temperature effect

The temperature effect on the self-assembly of fullerene over graphene has been examined by investigating the size of the fullerene assembly for three different temperatures 200, 300 and 400 K. The size of the fullerene assembly on the surface of graphene for the three different temperatures is determined from the time evolution of radius of gyration of all the 12 bucky balls and it is shown in figure 11 for the two simulated systems Single-gb and Double-gb. The rise in temperature enhances the self-assembly of fullerene. In the case of the Single-gb system, assembly of fullerene emerges at 18.6, 11.8 and 0.6 ns for the temperatures 200, 300 and 400 K, respectively. In the case of the Double-gb system, assembly of fullerene emerges at 2.8, 0.8 and 0.6 ns for the temperature 200, 300 and 400 K, respectively. This observed trend shows the influence of temperature on the formation of self-assembly

Figure 10. Distribution of COM distance between the bucky balls (300 K).

Figure 11. Effect of temperature on the self-assembly of fullerene.

of fullerene. Moreover at higher temperature (400 K), assembled fullerenes are compact in size. This may be due to the enhanced interactions between the bucky balls which might have placed them closer with the increase in temperature from room temperature.

3.6 Structure of graphene

The conformation of graphene sheet highly influences its mechanical, electrical and adsorption properties. So it is essential to examine the conformation of graphene sheet of graphene–fullerene nanocomposite. The conformation of graphene sheet of graphene–fullerene nanocomposite at room temperature can be identified from the variation of x -length and y -length of graphene with respect to time displayed in figure 12. A close inspection of figure 12 reveals the fluctuation in the length of the graphene sheets which is a signature of the curved surface. The curvature of graphene sheet is caused

Figure 12. Time evolution of length of graphene sheets (300 K).

Table 5. Length of graphene sheet (300 K).

Sl. no.	System	x length (Å)	y length (Å)
1	Single-gb	184.47 ± 2.56	168.34 ± 2.86
2	Double-gb		
	Sheet 1	172.59 ± 1.20	153.40 ± 1.80
	Sheet 2	172.61 ± 1.21	153.42 ± 1.80

by spontaneous bending of the sheet. The average x -length and y -length of the graphene sheet is shown in table 5.

In the case of two layer graphene–fullerene nanocomposite, there is not much difference between the length of two graphene sheets. This indicates their similar orientation and conformation with the same degree of curvature. But when we compare the length of single layer graphene and double layer graphene there is much difference. Single layer graphene has longer x -length and y -length. There is a difference of around 12 and 15 Å in x -length and y -length, respectively. This shows the enhanced conformational change and higher degree of curvature of single layer graphene than double layer graphene. As single layer graphene is free from the force of neighbouring graphene layer, it has enhanced conformational change. The fluctuations in the length of the two layer graphene might have been suppressed due to the domination of inter-sheet interactions. The higher degree of curvature of single layer graphene might have increased the mobility of the bucky balls moving on it. Goler *et al* [56] have reported the preferential chemisorption of hydrogen on monolayer graphene (grown on SiC(0001)) in the areas where the local curvature is maximally convex using scanning tunnelling microscopy technique.

The above determined and discussed structural features of the graphene–fullerene nanocomposite such as interaction energy, BE, size, spatial distribution, interparticle separation, self-assembly of fullerene, temperature effect, influence of

single and double graphene sheets, mobility and conformation may be harnessed in the design and development of the graphene–fullerene nanocomposite for the appropriate biological and technological applications.

4. Conclusions

The structural properties of the graphene–fullerene nanocomposite have been studied using MD simulation. The simulated graphene–fullerene nanocomposite has self-assembly of bucky balls on the surface of graphene. The stable structure of the graphene–fullerene nanocomposite has resulted from the intermolecular interactions between graphene and fullerene. The number of layers of graphene has influenced the structure of graphene–fullerene nanocomposite. The rise in temperature has enhanced the self-assembly of fullerene. The structure, size, interparticle separation, spatial distribution, mobility and conformation of the graphene–fullerene nanocomposite have been calculated and analysed. The graphene–fullerene nanocomposite may have enhanced new physicochemical properties. The distinctive molecular structure and the specific ordered arrangement of molecules within the graphene–fullerene nanocomposite and their emerging new synergistic properties may be utilized for the biological and technological applications. In the present work, pristine graphene sheets and C₆₀ fullerene molecules are simulated to study their self-assembly. This work can be further extended by simulating the different size fullerene molecules enclosed within the functionalized graphene sheets.

Acknowledgements

The author expresses her sincere thanks to SERB Fast Track Project [SR/FTP/PS-214/2012], New Delhi for the financial support. All the simulations were carried out in High Performance Computing Cluster at SASTRA Deemed University, Thanjavur, Tamil Nadu, India. The author thanks Dr L Ramya, School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur, Tamilnadu, India for her valuable suggestions.

References

- [1] Allen M J, Tung V C and Kaner R B 2009 *Chem. Rev.* **110** 132
- [2] Liao L, Peng H and Liu Z 2014 *J. Am. Chem. Soc.* **136** 12194
- [3] Sanchez V C, Jachak A, Hurt R H and Kane A B 2011 *Chem. Res. Toxicol.* **25** 15
- [4] Yavari F and Koratkar N 2012 *J. Phys. Chem. Lett.* **3** 1746
- [5] Liu J, Tang J and Gooding J J 2012 *J. Mater. Chem.* **22** 12435
- [6] Gong X, Liu G, Li Y *et al* 2016 *Chem. Mater.* **28** 8082
- [7] Hu M, Yao Z and Wang X 2017 *Ind. Eng. Chem. Res.* **56** 3477
- [8] Bao Q and Loh K P 2012 *ACS Nano* **6** 3677
- [9] Chee W K, Lim H N, Zainal Z *et al* 2016 *J. Phys. Chem. C* **120** 4153
- [10] Chung C, Kim Y-K, Shin D *et al* 2013 *Acc. Chem. Res.* **46** 2211
- [11] Dinadayalane T C and Leszczynski J 2012 Fundamental structural, electronic, and chemical properties of carbon nanostructures: graphene, fullerenes, carbon nanotubes, and their derivatives. In: *Handbook of computational chemistry* (Dordrecht: Springer) p 793
- [12] Dinadayalane T C and Leszczynski J 2010 *Struct. Chem.* **21** 1155
- [13] Hermanson G T 2013 *Buckyballs, fullerenes, and carbon nanotubes. Bioconjugate techniques*, 3rd edn (London, UK; Waltham, USA; San Diego, USA: Academic Press) Chapter 16, p 741
- [14] Goodarzi S, Da Ros T, Conde J *et al* 2017 *Fullerene: Mater. Today* **20** 460
- [15] Castro E, Garcia A H, Zavala G and Echegoyen L 2017 *J. Mater. Chem. B* **5** 6523
- [16] Popov A A, Yang S and Dunsch L 2013 *Chem. Rev.* **113** 5989
- [17] Coro J, Suárez M, Silva L S *et al* 2016 *Int. J. Hydrogen Energy* **41** 17944
- [18] Georgakilas V, Perman J A, Tucek J and Zboril R 2015 *Chem. Rev.* **115** 4744
- [19] Janani M, Srikrishnarka P, Nair S V and Nair A S 2015 *J. Mater. Chem. A* **3** 17914
- [20] Innocenzi P and Brusatin G 2001 *Chem. Mater.* **13** 3126
- [21] Mendes R G, Bachmatiuk A, Büchner B *et al* 2013 *J. Mater. Chem. B* **1** 401
- [22] Bakry R, Vallant R M, Najam-ul-Haq M *et al* 2007 *Int. J. Nanomed.* **2** 639
- [23] Yu D, Park K, Durstock M and Dai L 2011 *J. Phys. Chem. Lett.* **2** 1113
- [24] Spyrou K, Kang L, Diamanti E K *et al* 2013 *Carbon* **61** 313
- [25] Liu Z-B, Xu Y-F, Zhang X-Y *et al* 2009 *J. Phys. Chem. B* **113** 9681
- [26] Thirumalraj B, Palanisamy S, Chen S-M and Lou B-S 2016 *J. Colloid Interface Sci.* **462** 375
- [27] Guan J, Chen X, Wei T *et al* 2015 *J. Mater. Chem. A* **3** 4139
- [28] Gan T, Hu C, Sun Z and Hu S 2013 *Electrochim. Acta* **111** 738
- [29] Li Q, Hong L, Li H and Liu C 2017 *Biosens. Bioelectron.* **89** 477
- [30] Rather J A, Khudaish E A, Munam A *et al* 2016 *Sens. Actuators B: Chem.* **237** 672
- [31] Neek-Amal M, Abedpour N, Rasuli S N *et al* 2010 *Phys. Rev. E* **82** 051605
- [32] Lohrasebi A, Neek-Amal M and Ejtehadi M R 2011 *Phys. Rev. E* **83** 042601
- [33] Savin A V and Kivshar Y S 2012 *Sci. Rep.* **2** 1012
- [34] Becton M, Zhang L and Wang X 2014 *J. Nanomech. Micromech.* **4** B4014002
- [35] Mirzayev R, Mustonen K, Monazam M R *et al* 2017 *Sci. Adv.* **3** e1700176
- [36] Xu S, Fu H, Li Y *et al* 2016 *Phys. Chem. Chem. Phys.* **18** 10138
- [37] Feng J, Ding H and Ma Y 2015 *Carbon* **90** 34
- [38] Ozmaian M, Fathizadeh A, Jalalvand M *et al* 2016 *Sci. Rep.* **6** 21910
- [39] Mukhopadhyay T K and Datta A 2017 *J. Phys. Chem. C* **121** 10210
- [40] Mukhopadhyay T K and Datta A 2018 *ACS Appl. Mater. Interfaces* **10** 13805
- [41] Wu X and Zeng X C 2008 *Nano Lett.* **9** 250

- [42] Ojeda-Aristizabal C, Santos E J, Onishi S *et al* 2017 *ACS Nano* **11** 4686
- [43] Ullmann K, Coto P B, Leitherer S *et al* 2015 *Nano Lett.* **15** 3512
- [44] Laref S, Asaduzzaman A M, Beck W *et al* 2013 *Chem. Phys. Lett.* **582** 115
- [45] Wang M and Li C M 2011 *Phys. Chem. Chem. Phys.* **13** 5945
- [46] Lau C S, Sadeghi H, Rogers G *et al* 2015 *Nano Lett.* **16** 170
- [47] MacKerell A D, Banavali N and Foloppe N 2000 *Biopolymers* **56** 257
- [48] Sathe C, Zou X, Leburton J-P and Schulten K 2011 *ACS Nano* **5** 8842
- [49] Luo N, Weber J K, Wang S *et al* 2017 *Nat. Commun.* **8** 14537
- [50] Saikia N, Johnson F, Waters K and Pandey R 2018 *Nanotechnology* **29** 195601
- [51] Kraszewski S, Tarek M, Treptow W and Ramseyer C 2010 *ACS Nano* **4** 4158
- [52] Kraszewski S, Tarek M and Ramseyer C 2011 *ACS Nano* **5** 8571
- [53] Phillips J C, Braun R, Wang W *et al* 2005 *J. Comput. Chem.* **26** 1781
- [54] Verhagen T G A, Vales V, Kalbac M and Vejpravova J 2017 *Diamond Relat. Mater.* **75** 140
- [55] Saikia N, Jha A N and Deka R C 2013 *J. Phys. Chem. Lett.* **4** 4126
- [56] Goler S, Coletti C, Tozzini V *et al* 2013 *J. Phys. Chem. C* **117** 11506