DISTANCE BASED TOPOLOGICAL INDICES ON GRAPHENE AND MWCNT SAMPLES OBTAINED BY ELECTROLYSIS IN MOLTEN SALTS

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ABSTRACT

The interest for the very intensive studies and methods of structural characterization of graphene and MWCNT to date has resulted in many valuable contributions and amazingly wide application area. This work includes graph representation of these nanotubical structures obtained by electrolysis in molten salts using non-stationary current regimes, based on their low frequency region Raman spectra and XRD data. The spectroscopic data enables precise determination of the graphene samples' mean crystallite sizes, both vertical and in-plane, their number of layers, as well as studying the walls' diameters and performing an (n,m) assignment of nanotube samples. Using the graph representation and the chirality of the studied samples, different distance based topological indices (Wiener index, Balaban index, Sum-Balaban index, Haray index, etc.) have been evaluated in order to predict some index-related properties of the molecules.

INTRODUCTION

Electrochemical method is a proven low-cost method for a high-yield production of carbon based nanostructures, as are carbon nanotubes (CNT) and graphene [1,2]. Obtained carbon nanotubes' properties largely depend on their atomic structure, hence determination of CNT's diameter and/or chiral angle is essential. Accurate determination of chiral indices m, n enables calculations of any CNT's structural parameter. There are studies that suggest some methods of (m,n) assignment for SWCNTs, as well as for MWCNTs. However, precise determination becomes extremely complicated for more than three walls (layers) [4-7]. Graphene can be produced as a mixture of monolayers, bi-layers and multilayers (3–10 monolayers) in form of flakes or flat sheets [3]. Having highly unusual properties largely due to their structure makes structural characterization of these graphitic nanomaterials a very important activity as part of intensive studies and research. Graphene and MWCNT samples that are subject of this study were produced by electrolysis in molten salts using non stationary current regimes. Obtained graphene samples have non-uniform distribution of few layers (2-4), small in-plane mean crystallite size L_a within the range of 1.82 nm – 2.46 nm [8,9]. Obtained CNTs are multi-wall tubes having highly ordered structures and undetermined diameter and chirality. Therefore, this research is strictly focused to determination of outermost wall chiral indices and corresponding distance based topological indices of these graphitic nanostructures.

Experimental. Materials and techniques

In chemical graph theory QSAR and QSPR are often used terms derived from Quantitative Structure Property Relations and Quantitative Structure Activity Relations. QSAR and QSPR are regression models that relate a set of "predictor" variables to the power of the response variable.

In QSAR modeling, the predictors consist of physico-chemical properties or theoretical molecular descriptors of chemicals, while the QSAR response-variable could be a biological, pharmacological, medical, ecological, and/or some other activity of the chemicals.

Both QSAR and QSPR are showing the tendency of contemporary theoretical and mathematical chemistry, to predict the properties of a compound based on its molecule structure. The research in this field is mainly done by combining graph molecular descriptors and experimental results. They are using a simple method of representing molecules/structures as graphs. Each atom is presented as a vertex and the bonds between the atoms are the edges (links) in the graph.

In what follows, let G be a connected graph. By V(G) and E(G) the vertex and edge set of G are respectively denoted. Let k=|V(G)| and e=|E(G)|. Two vertices $u,v\in$V(G) being given, dist (u,v) is the distance from u to v in G. The degree (valence) of the vertex v is denoted by deg(v).

Most of the topological indices, also known as molecular descriptors, can be organized into two groups: distance based and degree based indices. It is important to notice that the graph representation of nanotubes and graphene are cubic (three regular graphs- all vertices are of degree three) or sub-cubic (all the vertices are of degree three except the vertices on the outer face). Therefore the degree based topological indices are not suitable for these types of structures. Hence, we are only considering distance based topological indices such as Wiener index, Harary index, Gutman index, Balaban index, and Sum-Balaban index.

The Wiener index is historically the first topological index. It was introduced in [10] and it is defined as the sum of distances between all pairs of vertices. Hence, for a graph G the Wiener index, W(G) is

$$W(G)=\sum_{u,v\in V(G)} \mathrm{dist}(u,v) \qquad 1)$$

This index is widely studied in chemistry and in pure mathematics. It has also found applications in sociometry and the theory of social networks. Based on the success of Wiener index, plenty of molecular descriptors have been developed afterwards.

The Harary index of a graph is defined as

$$H(G)=\frac{e}{e-k+2}\sum_{u,v\in V(G)}\frac{1}{\mathrm{dist}(u,v)} \qquad 2)$$

where the sum is over all pairs of distinct vertices of G. This index has been introduced independently by Plavšić et al. [11] and by Ivanciuc et al.[12] in 1993. It turned out that the performance of this index for chemical purposes is quiet modest, but on the other side the Harary index also appears in the study of complex networks.

The Balaban index was introduced by Balaban [13,14]. This topological index was used successfully in QSAR/QSPR modeling [15,16,17]. Balaban index J(G) of a graph G is defined as:

$$J(G)=\frac{e}{e-k+2}\sum_{uv\in E(G)}\frac{1}{\sqrt{w(u)w(v)}} \qquad 3)$$

where the sum is over all edges uv of G. For $x\in$ V(G), we have

$$w(x)=\sum_{y\in V}\mathrm{dist}(x,y) \qquad 4)$$

In [18] it was shown that Balaban index reduces the degeneracy of Wiener index for alcanes and provides much higher discriminating ability. Therefore, Balaban index is also called "sharpened Wiener index".

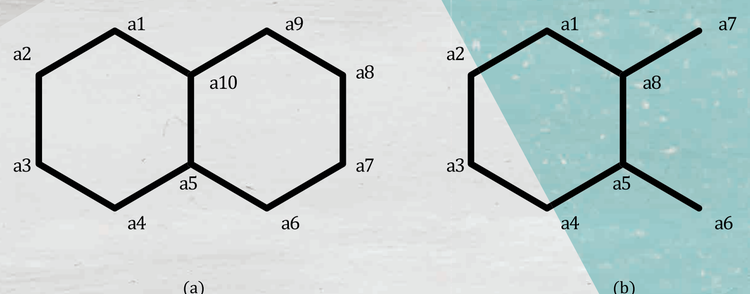
The Sum-Balaban index [19] is recently introduced modification of Balaban index and it is defined as:

$$SJ(G)=\frac{e}{e-k+2}\sum_{uv\in V(G)}\frac{1}{\sqrt{w(u)+w(v)}} \qquad 5)$$

Gutman index is another distance based topological index defined as

$$Gut(G)=\sum_{u,v\in V(G)} d(u)d(v)\mathrm{dist}(u,v) \qquad 6)$$

The results in this paper are motivated by [20] where the number of vertices at a given distance from a vertex u on infinite hexagonal tube is determined. Applying this result, the asymptotic value of Wiener, Gutman, Balaban, Sum-Balaban and Harary indices for nanotubes are obtained.



(a) (b)

Fig 1. Simple theoretical graphene layers

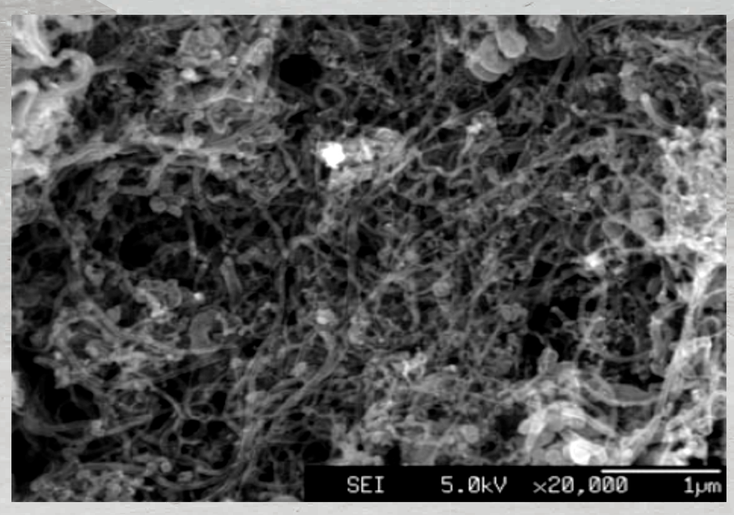
Assuming simple graphene layer is given (as shown in Fig 1a and Fig 1b), obtained distance based topological indices are given in Table 1. Observe that due to graph symmetry for graphene on Fig 1a it holds $w(a1)=w(a4)=w(a6)=w(a9)$, $w(a2)=w(a3)=w(a7)=w(a8)$, and $w(a5)=w(a10)$. Similarly for the graphene in Fig 1b, $w(a1)=w(a4)$, $w(a2)=w(a3)$, $w(a5)=w(a8)$, and $w(a6)=w(a7)$. This observation will significantly reduce the complexity of the calculations.

Table 1. Numerical values of distance based topological indices for graphene shown in Fig1.

	Wiener index W(G)	Balaban index J(G)	Sum-Balaban index SJ(G)	Harary index H(G)	Gutman index Gut(G)
Graphene in Fig 1a	109	2.14105	6.83647	22.4	489
Graphene in Fig 1b	62	0.26820	0.51736	16.16667	210

Clearly, from Table 1, all of the considered distance based topological indices are good in distinguishing these two graphene samples.

CNT sample considered for this study, having a nomenclature CNT – 3, is a multiwall tube, having an outermost diameter estimated to ~ 30 nm and a length ~ 5 μm. Part of its Raman spectrum is displayed on Fig 2B, showing of its D and G modes. The ratio of their intensities $I_D/I_G = 0.296$ is very low, which points to its highly ordered structure. The evident softening of the G-mode originates from the expansion of the inner layers which is unambiguously due to the inter-layer distance larger than 0.34 nm [6]. Furthermore, the G-mode having two components (G- and G+) being both narrow and symmetric identify the studied CNT as semiconducting chiral one. The latter will be used to narrow down the choice of the most probable chiral indices (m, n) assignment, as it must be satisfied that MOD(2m+n,3) = 1 or MOD(2m+n,3) = 2.



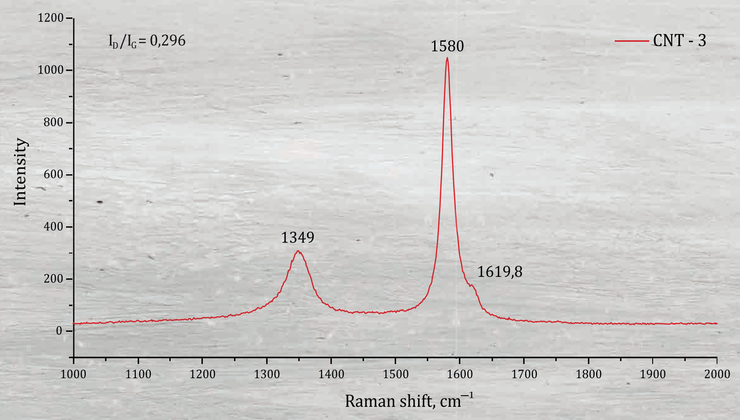


Figure 2. SEM image of CNTs obtained by electrolysis in molten salts (A); Raman spectrum D and G-modes display of CNT – 3 (B).

The well known relation between the diameter of nanotube and the vector defining its type d=78.3$\sqrt{(m^2+n^2+nm)}$ pm is used to get $m^2+n^2+mn=(d/78.3)^2$. To determine possible values of m and n for nanotubes with diameter $30nm\pm5nm$ the software Mathematica is applied.

Results and discussion

The obtained results are summarized with regard to closest values of $\tilde{A}=m^2+n^2+mn$ to $A=(d/78.3)^2$ ($\pm$ 2 pm^2) (Table 2). Additionally the values of distance based topological indices: Wiener index, Balaban index, Sum-Balaban index, Harary index and Gurman index for the nanotube with its most probable chiral index-assignments are obtained applying the software Mathematica (Table 3).

Table 2. Possible (m,n) assignment for a nanotube CNT - 3 with estimated diameter

Estimated diameter d (in nm)	A	Possible (m,n) assignment	$\tilde{A}$	MOD (2m+n,3)	
25	101943	(44,295)	101941	2	chiral semiconducting
		(95,261)	101941	1	chiral semiconducting
26	110261	(37,312)	110257	2	chiral semiconducting
		(123,253)	110257	1	chiral semiconducting
		(128,249)	110257	1	chiral semiconducting
		(176,207)	110257	1	chiral semiconducting
27	118906	(162,234)	118908	0	chiral metallic
28	127877	(66,320)	127876	2	chiral semiconducting
		(90,304)	127876	1	chiral semiconducting
29	137174	(43,347)	137179	1	chiral semiconducting
		(118,297)	137179	2	chiral semiconducting
30	146798	(12,377)	146797	2	chiral semiconducting
		(117,311)	146797	2	chiral semiconducting
		(172,267)	146797	2	chiral semiconducting
		(153,283)	146797	1	chiral semiconducting
		(165,273)	146799	0	chiral metallic
		(180,260)	146800	2	chiral semiconducting
31	156747	(218,239)	156747*	0	chiral metallic
32	167023	(54,379)	167023*	1	chiral semiconducting
33	177625	(122,347)	177627	0	chiral metallic
34	188553	(29,419)	188553*	0	chiral metallic
35	199808	(143,358)	199807	2	chiral semiconducting
		(0,447)	199809	0	zig-zag metallic

By * are denoted the exact matches of $\tilde{A}$ to A.

Possible assignments are considered with regard to $|\tilde{A}-A|<2$. Based on the results summarized in Table 3, there are eleven possible chiral indices assignment out of 23 satisfying such a condition, with only three exact matches of $\tilde{A}$ to A, where $|\tilde{A}-A|=0$, which points to precise agreement between the diameter and the proposed chiral indices: (218,239) to 31 nm, (54, 379) to 32 nm, and (29, 419) to 34 nm. However, both nanotubes (218,239) and (29,419) are metallic and hence the only exact match satisfying every condition is (54, 379). Furthermore, three more index assignments are eliminated for having the metallic property as well as the three other assignments for the diameters that deviate most from the approximated length of 30 nm and also not being an exact match. That leaves seven possibilities which are considered for further calculations, however it should be stressed that (54, 379) is the most probable assignment for the reasons previously discussed.

In order to evaluate distance based topological indices, the number of vertices/atoms in the nanotube is highly important. The vector (m,n) determines the diameter of the tube, but the distance between any two vertices depends on the length of the nanotube as well. The nanotube length is determined by the number of vertices. In our experiments the length of the obtained nanotube is evaluated to be 5000 nm. Using this information and the type of the nanotube the number of vertices is asymptotically determined. For that purpose the following formulas are used: the length of the translation vector, $\overrightarrow{T}$, T= $(\sqrt{3}d)/(d_R)$ where d_r=GCD($2m+n$,$2n+m$), GCD standing for the greatest common divisor. The translation vector $\overrightarrow{T}$ and the vector (m,n) determine a rectangular called *unit cell*. The number of vertices in each unit cell is N=$(4(m^2+n^2+mn))/d_R$ (for more details see [21]). The length of the translation vector and the length of the nanotube determine the number of (repeating) unit cells and hence the total number of vertices. The obtained results are presented in Table 3.

Table 3. Number of vertices in a nanotube of length 5000 nm

Diameter d (in nm)	(m,n) assignment	Length of the translation vector	Number of vertices (atoms) in a unit cell	Number of vertices/atoms in the nanotube
28	(66,320)	24249	255752	52684912
28	(90,304)	24248	255752	52684912
30	(12,377)	51961	587188	56370048
30	(117,311)	51961	587188	56370048
30	(172,267)	51961	587188	56370048
30	(153,283)	51961	587188	56370048
32	(54,379)	43323	408172	46939780

Now, using the results from Table 3, [20] and software Mathematica distance based topological indices can be asymptotically evaluated. The values of these molecular descriptors are given in Table 4. Here it is visible that these topological indices indeed distinguish the nanotubes.

Table 4. Values of distance based topological indices for nanotube CNT - 3 with most possible diameters and chiral indices assignment

Diameter d (in nm)	(m,n) assignment	W(G) $*10^{19}$	J(G)	SJ(G) $*10^{11}$	H(G) $*10^{-5}$	Gut(G) $*10^{20}$
28	(66,320)	6.31423	110.2	1.57031	10.35245	3.78854
28	(90,304)	6.18602	111.3361	1.60286	10.56701	3.71161
30	(12,377)	7.6744	110.6274	1.69965	9.75086	4.60464
30	(117,311)	6.9751	116.0405	1.87005	10.72846	4.18506
30	(172,267)	6.80032	117.5222	1.91811	11.00419	4.08019
30	(153,283)	6.84711	117.12	1.905	10.92899	4.10827
32	(54,379)	5.02548	103.8807	1.23514	10.32512	3.01529

CONCLUSIONS

This work's most important aim is determination of distance based topological indices of experimentally obtained carbon nanostructures as are graphene and CNTs. The studied samples are obtained with electrolysis in molten salts using non-stationary current regimes.

Several methods and techniques have been used to create an approach in assigning chiral indices to nanotubes having approximate values of their outermost diameter. The proposed approach enables determination of useful distance based topological indices for its unit cell alone and regardless of the nanotube's length. However, the calculations of the indices herein are given considering the previously estimated value of the nanotube's length. It is evident that the determined indices distinguish the nanotubes with regard to their chirality.

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