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Dedicated to Professor Liviu Literat, at his 80th anniversary

CLUJ POLYNOMIAL DESCRIPTION OF TIO_2 NANOSTRUCTURES

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ABSTRACT. Operations on maps are well known theoretical tools for transforming a given polyhedral tessellation. In this article, we propose a new method to design a titanium nanostructure. To describe the topology of such structures, we applied Cluj counting polynomial.

Keyords: *TiO_2 nanostructures, molecular design, polynomial description*

INTRODUCTION

After the discovery of carbon nanotubes many researchers addressed the question about the possible existence of nanotubular forms of other elements and they tried to obtain inorganic nanostructures [1-3]. Among numerous oxide nanostructures, the titanium nanotubular materials are of high interest due to their chemical inertness, endurance, strong oxidizing power, large surface area, high photocatalytic activity, non-toxicity and low production cost. The application of TiO_2 nanotubes to photocatalysis, in solar cells, as nanoscale materials for lithium-ion batteries and as gas-sensing material was discussed in the literature [4–10]. The nanotubes (TiO_2) were synthesized using various precursors [11–17], carbon nanotubes, porous alumina or polymer membranes as templates [8–24], fabrication by anodic oxidation of Ti [25–27], sol–gel technique [28–32] and sonochemical synthesis [33]. Models of possible growth mechanisms of titanium nanotubes are discussed [16, 17, 32] but the details of the atomic structure of the nanotube walls and their stacking mode are unknown. TiO_2 NTs are semiconductors with a wide band gap and their stability increases with increasing of their diameters. The numerous studies for the use of nanotubular titania in technological applications require a lot of theoretical studies of stability and other properties of such structures. Theoretical studies on the

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stability and electronic characteristics of TiO_2 nanostructures were presented in ref. [34, -36]. In the present paper we report a new method to design TiO_2 nanostructures using map operations, and then we describe their topology by the Cluj polynomial.

RESULTS AND DISCUSSION

Models and computational method

The titanium nanostructures can be achieved by map operations: the sequence consists of Du[Med(M)], applied on the polyhex tori or tubes (Figure 1).

(a) Du[Med(TUH(8,8))] (b) Du[Med(H832)]

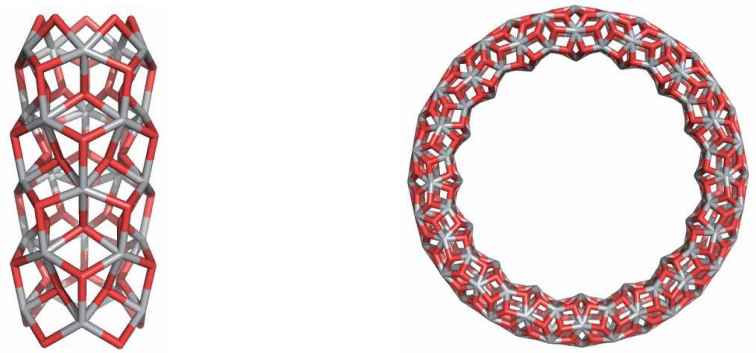

Figure 1. TiO_2 nanotube (a) and nanotorus (b).

A map *M* is a combinatorial representation of a (closed) surface [37,38]. Several transformations (*i.e.*, operations) on maps are known and used for various purposes.

Let us denote in a map: *v* – the number of vertices, *e* - the number of edges, *f* – the number of faces and *d* – the vertex degree. A subscript “0” will mark the corresponding parameters in the parent map.

Recall some basic relations in a map:

$$\sum d\, v_d = 2e \quad (1)$$

$$\sum s\, f_s = 2e \quad (2)$$

where v_d and f_s are the number of vertices of degree *d* and number of *s*-gonal faces, respectively.

Medial Me

Medial is achieved by putting new vertices in the middle of the original edges [38]. Join two vertices if the edges span an angle (and are consecutive within a rotation path around their common vertex in *M*). Medial is a 4-valent graph and *Me*(*M*) = *Me*(*Du*(*M*)), as illustrated in Figure 2. The transformed map parameters are:

$$Me(M): \quad v = e_0;\ e = 2e_0;\ f = f_0 + v_0 \tag{3}$$

The medial operation rotates parent *s*-gonal faces by π/s. Points in the medial represent original edges, thus this property can be used for topological analysis of edges in the parent polyhedron. Similarly, the points in dual give information on the topology of parent faces.

(a) (b)Me[TUH(8,4)] (b)Me[H(8,8)]

Figure 2. Medials of a polyhex nanotube.

Dual Du

The dualization of a map starts by locating a point in the center of each face. Next, two such points are joined if their corresponding faces share a common edge. It is the (Poincaré) *dual Du*(*M*). The vertices of *Du*(*M*) represent the faces of *M* and *vice-versa* [38].

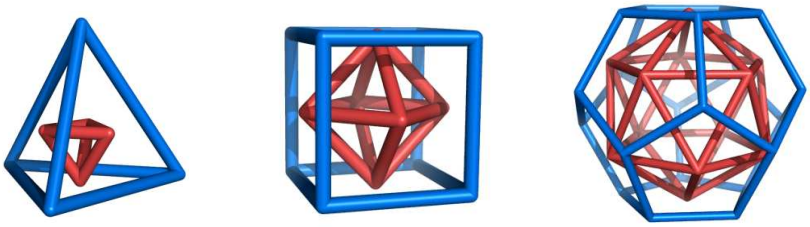

Figure 3. The duals of the Platonic polyhedra.

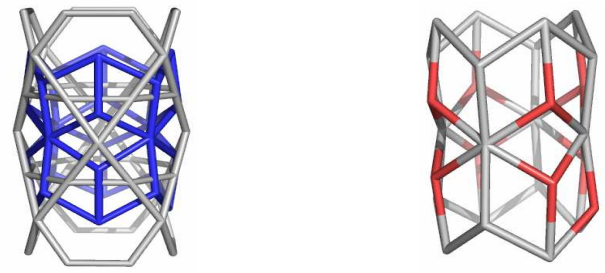

Figure 4. The dual of medial of a polyhex nanotube.

In the transformed map, the following relations exist:

$$Du(M):\ v = f_0;\ e = e_0;\ f = v_0 \tag{4}$$

Dual of the dual returns the original map: *Du*(*Du*(*M*)) = *M*. Tetrahedron is self dual while the other Platonic polyhedra form pairs: *Du*(Cube) = Octahedron; *Du*(Dodecahedron) = Icosahedron (Figure 3). The dual of medial of a polyhex nanotube will give a (4(3,6)) net which essentially correspond to the TiO2 lattice (Figure 4).

Cluj polynomial

Cluj polynomials are defined on the basis of Cluj matrices as:

$$CJ(G,x) = \sum_k m(G,k)\cdot x^k \tag{5}$$

They count the vertex proximity of the vertex *i* with respect to any vertex *j* in *G*, joined by an edge $\{p_{e,i}\}$ (the Cluj-edge polynomials) or by a path $\{p_{p,i}\}$ (the Cluj-path polynomials), taken as the shortest (distance DI) or the longest (detour DE) paths. In Equation (5), the coefficients *m*(*G*, *k*) are calculated from the entries of Cluj matrices.

The summation runs up to the maximum $k = |\{p\}|$ in *G*.

A Cluj fragment, [39-43] $CJ_{i,j,p}$, collects vertices *v* lying closer to *i* than to *j*, the endpoints of a path *p*(*i*,*j*). Such a fragment collects the vertex proximity of *i* against any vertex *j*, joined by the path *p*, with the distances measured in the subgraph $D_{(G-p)}$, as shown in the following equation:

$$CJ_{i,j,p} = \left\{v \middle| v \in V(G);\ D_{(G-p)}(i,v) < D_{(G-p)}(j,v)\right\} \tag{6}$$

In graphs containing rings, more than one path could join the pair (*i, j*), resulting in more than one fragment related to *i* (with respect to *j* and a given path *p*). The entries in the Cluj matrix are taken, by definition, as the maximum cardinality among all such fragments:

$$\mathbf{[UCJ]}_{\boldsymbol{i,j}} = \max_{p} \left| CJ_{i,j,p} \right| \tag{7}$$

In trees, due to the unique nature of paths joining any two vertices $CJ_{i,j,p}$ represents the set of paths going to *j* through *i*. In this way, the path *p*(*i,j*) is characterized by a single endpoint, which is sufficient for the unsymmetrical matrix UCJ. When the path *p* belongs to the set of distances *DI*(*G*), the suffix DI is added to the name of matrix, as in **UCJDI**. When path *p* belongs to the set of detours *DE*(G), the suffix is DE. The Cluj matrices are defined in any graph and, except for some symmetric graphs, are unsymmetrical and can be symmetries by the Hadamard multiplication with their transposes:

$$\mathbf{SM_p = UM \bullet (UM)^T} \tag{8}$$

If the matrices calculated on edges (*i.e*., on adjacent vertex pairs) are required, the matrices calculated from paths must be multiplied by the adjacency matrix **A** (which has the non-diagonal entries of 1 if the vertices are joined by an edge and, otherwise, zero)

$$\mathbf{SM_e = SM_p \bullet A} \tag{9}$$

The Cluj polynomials published previously [44] referred to some partitions of the Cluj matrices given by the layer/shell matrices, and provide no direct interpretation of the counting content.

The polynomial coefficients are counted from the Cluj matrices by the TOPOCLUJ software program [45] and also by a simple routine for collecting the entries in the unsymmetrical matrices **UCJ**. In the case of the $CJDI_e$ polynomial, an orthogonal edge-cutting procedure can be used [46]. The same procedure has been used by Gutman and Klavžar to calculate the Szeged index of polyhex graphs [47].

Cluj polynomial in Tio_2 nanotori

Cluj polynomial in non-twisted toroidal TiO_2 structures is composed by two terms, according to the proximities at the two ends of the edges (in a bipartite graph), which are topologically equivalent. Examples and formula for calculating CJ polynomial are given in Table 1. Observe there is no difference in CJ polynomial for the two different embeddings: H and V, in Diudea's nomenclature [48].

Table 1. Data for the non-twisted toroidal TiO_2 structures and analytical formula of Cluj CJ_e

Tori H	CJ_e Polynomial	ToriV	CJ_e Polynomial
H[10,10]	$300x^{70}+300x^{80}$	V[10,10]	$300x^{70}+300x^{80}$
H[10,20]	$600x^{145}+600x^{155}$	V[10,20]	$600x^{145}+600x^{155}$
H[8,8]	$900x^{220}+900x^{230}$	V[10,30]	$900x^{220}+900x^{230}$
H[12,12]	$192x^{44}+192x^{52}$	V[10,50]	$1500x^{370}+1500x^{380}$
H[10,60]	$432x^{102}+432x^{114}$	V[10,70]	$2100x^{520}+2100x^{530}$

$$CJ_e(G, x) = b_a \cdot x^{e_{ka}} + b_b \cdot x^{e_{kb}}$$

$$e_{ka} = e_1 \cdot k + (k-1) \cdot (c/2)$$

$$e_{kb} = e_{ka} + c$$

$$e_1 = c^2 - (c/2) \cdot (c/2+1)$$

$$b = 3 \cdot c \cdot n = b_a = b_b$$

$$k = n/c$$

CONCLUSIONS

A new method for designing TiO_2 nanotubular structures, based on map operations, was proposed. Cluj polynomial description proved to be a good tool for searching the topology of a nanostructure, particularly nanostructures of titania. Omega polynomial description of such nanostructures will be presented in a future paper.

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