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Geometrical Modelling of Cubic Zirconia Nanosheet

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ABSTRACT

Computational modeling of cubic zirconia nano sheet was conducted in order to determine relevant geometrical parameters required for further analysis and as precursor for generation of nanotubes. The task was achieved with better output by expansion of primitive cell to higher axial range in comparison to surface cleaving of zirconia super cells on (111) miller indices using Crstalmaker. The single layered nano sheet formed is composed of hexagonal units made from bonds of zirconium and oxygen atoms. Output from the optimized structure of the nano sheet was used to obtain geometrical details for the hexagonal unit and Zr-O bond. Models were produced for (5, 0), (5, 5), (10, 0) and (10, 10) nano sheets and also for those to be used to produce zirconia nanotubes with the specific configurations. The nanosheets obtained can be exported with atomic coordinates and subsequently used as models for rolling zirconia nanotubes and simulation of required properties such as structural/mechanical, thermal, electronic, optical and others.

1. Introduction

Recently, significant progress has been achieved in various areas related to the synthesis and study of different nanostructure materials containing zirconia (ZrO_2) in different phases [1-6]. Specific interest has been paid to zirconia nanotubes (ZNT) because of their existing and potential applications, such as host matrix for optical functional materials, components of O_2 sensors, part of solid oxide fuel cells, as catalysts support and others [7-10].

Successful synthesis of ZNT has been reported using mainly the template-assisted depositions and direct anodization methods [11-15]. But a review of the different ZNT synthesized shows variations in morphology depending on method and conditions of fabrication [16]. This makes it difficult and sometimes impossible to characterize the structure and/or properties of ZNT due to the dependence of their properties on size and nano-structure [17]. Since direct experimental measurements are limited due to sizes of materials involved, the theoretical approach provides a reliable alternative.

The theoretical approach is based on computational simulation and can be divided into two main categories: the atomistic approaches and continuum mechanics approaches. The atomistic approaches are useful in solving problem related to molecular or atomic motions, but enormous computational tasks are required leading to limits in their scope. The continuum mechanics approaches are conducted using the concepts of classical continuum mechanics and continuum shell modelling and can be used to compute both static and dynamic properties with emphasis on geometrical and structural modelling of materials [18].

Simulation of inorganic nanotubes (INT) is based on the same concepts used for carbon nanotubes (CNT) where the nanotubes are assumed to be formed by rolling up of nano sheet (NS) to form a hollow cylinder and can be single or multi walled. For CNT, the basic structural unit is a single atomic layer, known as graphene [18, 19]. Majority of INT are of the form MX_2 (M=transition metal, X= S, Se, O). The basic structural unit of these INT is a triple layer sheet, consisting of a layer of transition metal cations and sandwiched between layers of anions [20]. WS_2 NT was the first MX_2 NT discovered in 1992, soon followed by MoS NT in 1993 and thereafter by others [21].

It should be noted that in NS, two of their dimensions are not confined to nano scale and are extremely thin films with thickness less than 100 nm. They can be deposited on a substrate (nano films), free standing (nano sheets), multi-layer structures (nano laminates) or integrated in a surrounding matrix material. NS can be metallic, ceramic or polymeric and used as single layer or multilayer structures [22].

From information available, theoretical studies of zirconia NS (ZNS) and ZNT are presently lacking or minimal [16]. Therefore, in this study an attempt is made to understand the relation between bulk ZrO_2 and ZNS made from cubic polymorph. More emphasis is on structural properties of sheets cleaved from ZrO_2 bulk in order to obtain details of the geometry of the basic units of ZNS required for simulation of ZrO_2 NT.

2. Experimental Methods

2.1 Computational Details

ZrO_2 slabs were generated from the cubic phase and considered as precursors for the ZNS. This require modelling the unit cell of ZrO_2 using a crystal and molecular structures software, CrystalMaker. The structural parameters used were obtained from earlier studies conducted as summarized in Table 1.

Table 1 Structural Parameters for Unit Cell of Cubic ZrO_2 [23]

Parameter	Value
Lattice distance (a=b=c)	5.0945 Å
Lattice angle (α=β=γ)	90°
Unit cell volume	31.84 Å^3
Space Group	*Fm*^{3}*m* (No. 225)
Coordination Number	
Zr	8
O_2	4
Atomic Coordinates (origin)	
Zr	(0,0,0)
O_2	(0.25,0.25,0.25)

Thereafter relevant tools in CrystalMaker were used to obtain structural details of ZrO_2 such as bond parameters, miller indices, d-spacing, unit cell volumes etc. Super cells with different configurations were made. Earlier study indicates that the cubic crystal has three types of non-equivalent low index surfaces: (001), (110) and (111). The (001) is

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just a special case of the surface for the less symmetric tetragonal phase. Thus only (110) and (111) faces were considered. NS are labelled according to the following notations: *pxxLn* where P is the first letter of the parent phase, xxx is the miller index, L is the type of 2D lattice (r – rectangular, c – centred rectangular, s – square, h – hexagonal) and n is the number of ZrO_2 after relaxation or reconstruction [16]. Based on the aforementioned notation, the slabs generated are C110r2, C111h1 and C111h2. Super cells of these slabs were made in order to obtain NS, which can be folded to form NT with required or specific dimensions by cleaving the super cell with specific miller index.

3. Results and Discussion

From lattice parameters of bulk ZrO_2 available [23], the unit and primitive cells were modelled; thereafter the unit cell was then cleaved to obtain the hexagonal structure and Zr-O bond as shown in Fig. 1.

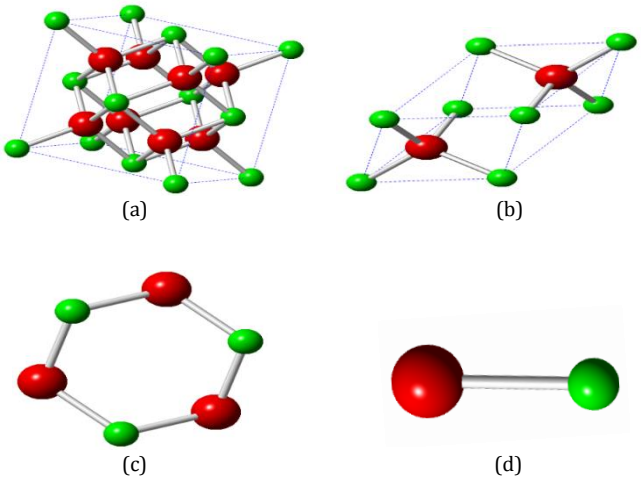


Fig. 1 a) Unit Cell; b) primitive cell; c) Hexagonal structure; and d) Zr-O bond of Cubic ZrO_2 (Zr = green or light; O_2 = red or darker)

The hexagonal unit was found out to be regular as distances of all sides were measured and equal to the Zr-O bond length; this was further confirmed by measuring the distances between opposite Zr atoms and opposite O_2 atoms and both were found to be 3.599 Å. Detail of the geometrical parameters of Zr-O bond is summarized in Table 2.

Table 2 Geometrical parameters of Zr-O bond.

Parameter	Value
Radius of O_2 atom (Å)	1.21
Radius of Zr atom (Å)	0.86
Zr-O bond length (Å)	2.221
Zr-O bond diameter (Å)	0.170
Zr-O bond area (Å^2)	0.0227
Zr-O bond volume (Å^3)	0.0501

It was observed that C110r2 have different bond lengths, d-spacing and densities when compared with C111h1 and C111h2 as was also noted in other studies [16]. Thus further analysis was based on the C111h1 model of the cubic ZrO_2.

The dimension of NS depends on the type of NT to be rolled or folded. The structure of a NT is specified in terms of the chiral numbers (n, m) or the chirality vector (C_h) inclined at an angle θ [18],

$$C_h = \mathbf{n}a_1 + \mathbf{m}a_2. \quad (1)$$

$$\theta = \frac{\sqrt{3}\,n}{2m+n}. \quad (2)$$

where a_1 and a_2 are the basic vectors of the hexagonal lattice as illustrated in Fig. 2.

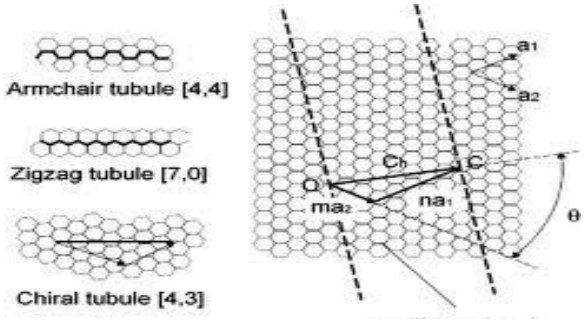


Fig. 2 Schematic diagram of a hexagonal NS [25]

The NS are classified into three groups named as zigzag (n, 0), θ = 0; armchair (n, n), θ = 30°; and chiral (n, m), m≠n≠0. The relationship between radius of NT, length of NT and integers n, m is expressed as [26]:

$$r = \frac{\sqrt{3}\,L}{2\pi}\sqrt{(n^2 + m^2 + mn)}. \quad (3)$$

Eq. 1, Eq. 2 and Eq. 3 were used to compute the details of ZNS required for various configurations of ZNT as listed in Table 3, where W_1 and W_2 are the width of NS using CrystalMaker and Nanotube Modeler respectively, L_s is length of ZNS and r is the radius of the NT to be formed.

Table 3 Geometrical parameters for ZNS

Type (n,m)	W_1 (Å)	W_2 (Å)	L_s (Å)	r (Å)	Atoms	Bonds
(5,5)	33.3	33.32	15.42	0.53	90	120
(5,0)	19.2	19.23	5.14	0.31	50	61
(0,5)	19.2	19.23	5.14	0.31	50	62
(10,10)	66.6	66.63	61.68	1.06	660	953
(10,0)	38.5	38.47	20.56	0.61	130	174
(0,10)	38.5	38.47	20.56	0.61	130	174
(14,14)	93.3	93.28	120.9	1.49	1797	2633
(14,0)	53.9	53.86	40.3	0.86	350	492
(0,14)	53.9	53.86	40.3	0.86	350	492
(18,18)	120	119.9	199.8	1.91	3796	5597
(18,0)	69.2	69.24	66.61	1.10	738	1060
(0,18)	69.2	69.24	66.61	1.10	738	1060
(5,2)	24.0	24.02	8.02	0.38	32	38
(10,7)	56.9	56.93	45.03	0.91	404	572
(8,5)	43.7	43.69	26.52	0.70	184	254
(14,11)	83.5	83.49	96.84	1.33	1266	1861

Various supercells were modeled from the data in Table 3 and the layers cleaved in order to obtain appropriate NS. As an illustration, the 5x5x5 super cell is shown in Fig. 3. The site have 1500 atoms, 6912 bonds within and with the next nearest neighbours (NNN) and 14.8086 Å as d-spacing.

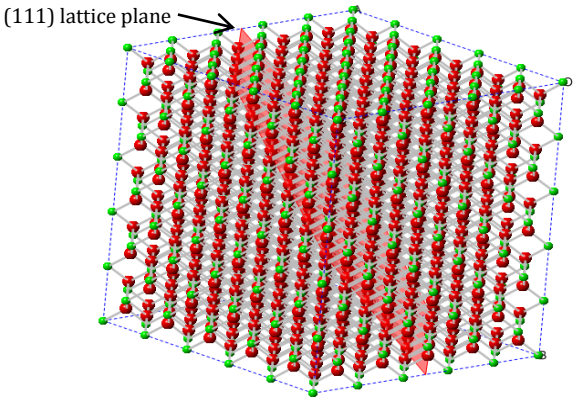
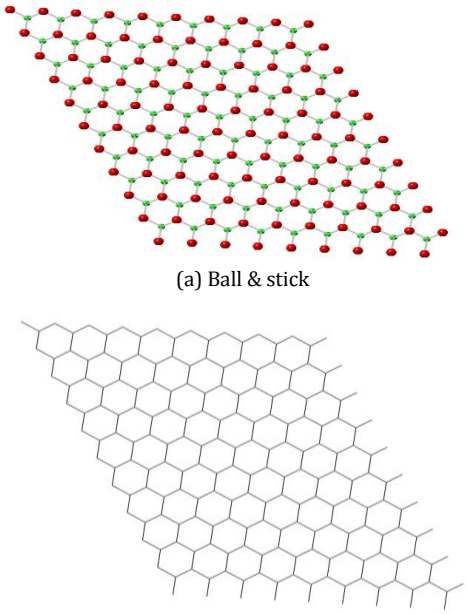


Fig. 3 A 3D view of the 5x5x5 super cell with lattice plane along (111) miller index.

The atoms and bonds on the selected lattice plane with 111 miller index were separated from the super cell to obtain the surface shown in Fig. 4.



(a) Ball & stick

(b) Wire frame

Fig. 4 ZrO_2 Nano sheet from 5x5x5 super cell in a) Ball & stick and b) wire frame models

It was observed that dimension of the NS was not the same as the value computed in Table 3. This is because the cleaving was possible along the diagonal axes as assumed during computation and also O_2 terminated sheet was preferred leading to reduction in dimension, as it has been established that metallic terminations as a rule make the surface unstable to oxidation [26]. The dimensions obtained were validated by using Nanotube Modeler as indicated by the NS width (W_1 and W_2) in Table 3.

Variations in some geometrical parameters were observed in types NS and ZNT as illustrated in Fig. 5; it should be noted that on the configuration axes, 1 represent armchair, 2 for zigzag and 3 for chiral.

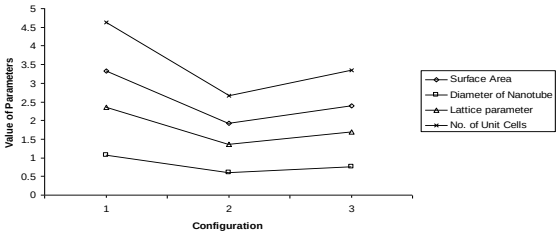


Fig. 5 Variation of some parameters for different types of ZrO_2

The armchair has higher geometrical parameters and zigzag the lowest as discovered in earlier studies [22-26].

But the models generated by CrystalMaker cannot be exported directly to ANSYS for further simulation in order to obtain specific mechanical properties of ZNS and ZNT. As an alternative, information about the models generated in CrystalMaker were saved as text files having the coordinates of atoms and all its connectivity. The data was thereafter exported to ANSYS using appropriate codes of APDL by taking atoms as nodes and bonds between atoms as elements [27].

4. Conclusion

The ZrO_2 NS is the basic unit for forming NT and was modeled using appropriate tools. The models proposed in this work provided various insights on the structural and geometrical properties of ZNS. The unit cell of ZrO_2 was developed based on various atomic data available which was transformed to form super cells. Thereafter, the basic hexagonal unit of the Nano sheet and geometrical parameters of the Zr-O bond were obtained. From 5x5x5 super cell, a surface of the ZrO_2 NS was cleaved along the (111) and (110) miller indices. The fractional coordinates of the atoms on the surface generated were exported for further simulation in order to obtain specific mechanical properties.

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