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## <sup>1</sup> Structural, Electronic, Vibrational, and Topological Analysis of <sup>2</sup> Single-Walled Zinc Oxide Nanotubes

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7 Supporting Information

ABSTRACT: Single-walled armchair and zigzag ZnO nanotubes 8 (SWZnONTs) have been studied via periodic computational simulations 9 based on density functional theory with the B3LYP, HSE06, PBE0, 10 and PWGGA functional and all-electron basis set. The influence of the 11 diameter of the nanotubes was carried out with respect to the bond length 12 (Zn-O), bond angles (Zn-O-Zn), energy strain, band gap, density of 13 states (DOS), band structures, vibrational analysis, and topological analysis 14 of the electron density according to the quantum theory of atoms in mole-15 cules applied to the solid state. Its nanotubes properties were compared 16 17 with the ZnO bulk and (0001) monolayer surface. The topological analysis, infrared and Raman spectra, and its vibrational modes at increasing 18 diameter are reported for the first time. Owing to these analysis, both 19 chiralities with large diameter can be used interchangeably in semi-20 conductor applications. These theoretical models can be extended to study 21



further issues, such as the effects caused by the addition of dopant and the interaction of molecules inside and/or outside of the nanotube.

### 24 INTRODUCTION

25 Owing to its electronic and electro-optical properties, zinc 26 oxide (ZnO) is widely used in technological applications. The 27 direct wide band gap energy (3.37 eV) and large excitation 28 binding energy (60 meV) enable its application in diodes, tran-29 sistors, and energy conversion systems such as solar cells and 30 transparent conducting oxides.<sup>1,2</sup> The structure and morphology 31 of ZnO are critical for the atomic-scale growth of nanomateri-32 als.<sup>1,2</sup> Nanostructures have increased the range of potential 33 application of ZnO; in particular, nanotubes, which are one-34 dimensional (1D) nanostructures, can be obtained using different 35 methods of synthesis.

The first observation of the multiwall carbon nanotubes was r credited to Iijima,<sup>3</sup> and in 1993, single-walled nanotubes were found by Iijima<sup>4</sup> and concurrently by Bethune.<sup>5</sup> Depending on how the sheet is wrapped, different nanotubes with singular properties can be obtained, thus opening new possibilities for further applications. These structures can be classified according to three main classes (based on chirality): armchair, zigzag, and chiral. The nanotube properties may change significantly depending on the chirality; for instance, armchair carbon nanotubes are always metallic, while the zigzag type can have a metallic or semiconducting character.<sup>6</sup>

47 Carbon nanotubes have been applied in different areas, but 48 owing to the dependence of their electronic properties on their 49 chirality, their application in semiconductors has not been 50 very successful. For this reason, in recent years, other plausible alternatives, such as inorganic nanotubes, have received increasing attention; in particular, inorganic nanotubes composed of 52 metal oxides with morphology similar to that of carbon nanotubes have been explored. Among the several experimental 54 techniques adopted to obtain inorganic nanotubes, a widely 55 used method involves the material deposition onto an anodized 56 aluminum oxide membrane template by using a collimated 57 electron beam evaporation source.<sup>7</sup> 58

The synthesis of single-walled ZnO nanotubes (SWZnONTs) 59 is influenced by the control of the synthesis route,<sup>8</sup> which leads 60 to the improvement of the electrical and optical properties and 61 is typically realized by using metal—organic chemical vapor 62 deposition, also utilized by Xu et al.<sup>9</sup> to grow SWZnONTs on 63 a Si substrate. Martinson et al.<sup>9</sup> used ZnO nanotubes as 64 photoanodes in dye-sensitized solar cells, comparing them with 65 other ZnO-based devices. The solar cells showed significant 66 photovoltage and fill factor values and an efficiency up to 1.6%. 67

From a theoretical point of view, the three types of nano- 68 tubes can be easily obtained and simulated by adopting dif- 69 ferent techniques and theories. The simplicity to obtain a 70 nanotube can be theoretically estimated by calculating the 71 strain energy ( $E_s$ ), which considers the energy necessary to 72 "wrap" a nanotube; thus, lower  $E_s$  values correspond to simple 73

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<sup>74</sup> nanotube fabrication. Notably,  $E_s$  can be calculated according to <sup>75</sup> the equation  $E_s = E_{\text{nanotube}}/(n \text{ atoms}) - E_{\text{slab}}$ , where  $E_{\text{slab}}$  is the <sup>76</sup> surface energy,  $E_{\text{nanotube}}$  is the energy of the nanotube, and *n* is <sup>77</sup> the number of atoms of the nanotube. As a standard, some <sup>78</sup> authors use the  $E_s$  values of the carbon nanotubes to compare <sup>79</sup>  $E_s$  of other nanotubes, as carbon nanotubes are easily obtained. <sup>80</sup> Wang et al.<sup>10</sup> analyzed the stability and electronic structure <sup>81</sup> of SWZnONTs using density functional theory (DFT) with <sup>82</sup> the local density approximation (LDA) functional; they showed <sup>83</sup> that the ZnO nanotube structure was very stable, experi-<sup>84</sup> mentally attainable, and had smaller values of  $E_s$  than other <sup>85</sup> nanotube structures reported in the literature, such as boron <sup>86</sup> nitride and gallium nitride.

Concerning the stability, Shen et al.<sup>11</sup> studied SWZnONTs with a small diameter and compared them with nanobelts and nanowires. The analyzed nanotubes were more stable than other nanostructures but less stable than nanotubes with larger diameters.

Mirnezhad and co-workers<sup>12</sup> investigated the size and or chirality dependence of the mechanical properties of ZnONTs of for four different adsorption positions of the H atom. Poisson's ratio and Young's moduli were determined via DFT with LDA of and showed that Young's modulus of the armchair nanotube was higher than those of the zigzag and chiral nanotubes.

Yan Su and co-workers<sup>13</sup> studied the adhesion of Pd nano-99 clusters on ZnONTs and the adsorption of probe gas molecules 100 on the outside, or inside, wall of ZnO and Pd/ZnONTs using 101 generalized gradient approximation (GGA). This study showed 102 that the adsorption presents high energy inside the nanotube. 103 Molecular dynamics were performed to simulate the struc-104 tural properties of zigzag, armchair, and chiral SWZnONTs.<sup>14</sup> 105 After relaxation, all nanotube structures perfectly retained their 106 ideal tube structures at 1 and 300 K, when periodic boundary 107 conditions were used. On the other hand, when the strain was 108 applied, the armchair and chiral nanotubes frequently assumed 109 hexagonal and square geometries, while the zigzag nanotube 110 assumed a hexagonal geometry.

Lacivita et al.<sup>15</sup> analyzed the bulk and (6,6) zigzag nanotube properties using DFT with PBE, B3LYP, LDA functional, and Hartree–Fock (HF) theory. They reported that for LDA and HPBE the band gap of the nanotube was more than twice that of the bulk while for B3LYP, the value obtained for the nanotube kas about 50% higher than that of the bulk HF overestimated to y15%. The vibrational modes of (n,n) nanotubes were also las calculated, but no direct correspondence was found in the vibrational spectrum of the monolayer surface.

Armchair and zigzag nanotubes were studied by Moraes et 121 al.<sup>16</sup> with respect to length, diameter, and band gap using the 122 AM1 semiempirical method; the results were then compared 123 with those obtained with RHF/3-21G level. The band gap in-124 creased with the nanotube diameter and reached values of 125 almost 9.0 eV for armchair and 1.0 eV for zigzag nanotubes. 126 However, for zigzag nanotubes using AM1, a variation of the 127 gap values appeared. Compared with other theoretical and 128 experimental works, these results appeared overestimated.

<sup>129</sup> Wang and co-workers<sup>10</sup> calculated the Zn–O bond length, <sup>130</sup>  $E_{sr}$  and band gap for three types of SWZnONTs using GGA <sup>131</sup> with exchange-correlation functional parametrized by PBE and <sup>132</sup> showed that  $E_s$  decreased with the increase of the diameter <sup>133</sup> nanotubes, while the band gap increased for all nanotubes to <sup>134</sup> ~1.9 eV, concluding that zigzag nanotubes were more stable <sup>135</sup> than others. 162

These theoretical studies present different results and con- 136 clusions, indicating that this research area is still quite open and 137 indefinite. Few theoretical studies have been devoted to ZnO 138 nanotubes, and in general, these works report models for 139 nanotubes of small diameter. Therefore, it is crucial to acquire 140 knowledge and understanding by comparing the atomic-scale 141 structural and electronic properties of this class of nanoma- 142 terials with the well-known properties of bulk and surfaces. 143

In this paper, periodic computational simulations are 144 reported, based on DFT with the B3LYP, HSE06, PBE0, and 145 PWGGA functional and all-electron basis set to investigate the 146 structural, electronic, and vibrational properties of wurtzite 147 ZnO single-walled armchair (n,n) and zigzag (n,0) nanotubes. 148 A detailed study on the influence of the diameter of the nano- 149 tubes was carried out with respect to the bond length (Zn-O), 150 bond angles (Zn-O-Zn), energy strain, band gap, density 151 of states (DOS), band structures, and vibrational analysis. 152 A topological analysis of the electron density,  $\rho(r)$ , was con- 153 ducted according to the quantum theory of atoms in molecules 154 (QTAIM) as developed by Bader<sup>17</sup> and implemented in the 155 TOPOND code<sup>18</sup> for crystalline systems by Gatti.<sup>19,20</sup> The 156 nanotubes properties were compared with the ZnO bulk and 157 (0001) monolayer surface. 158

The nanotube models can be extended to study further 159 issues, such as the effects caused by the addition of dopant and 160 the interaction of molecules. 161

### COMPUTING METHOD AND MODELS

All computational simulations of SWZnONTs were performed 163 by periodic DFT using the CRYSTAL14 software.<sup>21</sup> CRYSTAL 164 uses a Gaussian-type basis set to represent crystalline orbitals as 165 a linear combination of Bloch functions defined in terms of 166 local functions (atomic orbitals). The zinc and oxygen centers 167 were described by 86-411d31G<sup>22</sup> and 8-411d1,<sup>23</sup> respectively. 168

The selected basis set is due to the fact that these have been 169 used previously,<sup>24,25</sup> however, another available combination 170 of basis set for Zn and, O atoms were tested and evaluated 171 preliminarily. The choice of this basis set is considering the best 172 approximation to the experimental band gap energy, lattice and 173 internal parameters. 174

A very large grid with 99 radial points and 1454 angular 175 points was adopted in the DFT integration. An overview of 176 the algorithms used in the introduction of the DFT in the 177 CRYSTAL computer code is presented by Towler and co- 178 workers<sup>26</sup> and more details can be found in CRYSTAL user 179 manual.<sup>21</sup> The level of accuracy in evaluating the infinite 180 Coulomb and HF exchange series is controlled by five param- 181 eters,  $T_i = 1, 2, 3, 4$  and 5, such that two-electron contributions 182 are neglected when the overlap between atomic functions is 183 below  $10^{-T_i}$ . For our calculations  $T_i$  have been set to 10, 10, 10, 184 20, and 40. The shrinking factor (Pack-Monkhorst and 185 Gilat net) was set to 8, corresponding to 78 independent k 186 points in the irreducible part of the Brillouin zone. For the 187 surface calculations, the k-points mesh belongs to the xy-plane, 188 whereas for nanotube calculations the k-points mesh acts on 189 the periodic direction, i.e., x direction. The choice of com- 190 putational parameters can affect the results and quality of 191 calculations. When more k-points are used, the sensitivity 192 of the total energy becomes smoother. In particular, the results 193 related to strain energy or surface energy can be sensitive to 194 the convergence of total energy. This is an important step 195 to the acknowledge the effect on the relevant quantities and 196 properties. 197

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In some cases, the surface energy can be modified and lead to roneous conclusion about relative stability of surfaces when energy of the K-grid does not present a smoother behavior. The same energy of nanotubes and strain energy. Therefore, the K-grid should be larger enough to have good cancellation of errors.

The band structures were obtained for 100 K points along the appropriate height-symmetry paths of the adequate Brillouin corresponding electronic structure. The choice of the theoretical exploration of these systems is based on previous works by our research group.<sup>27,28</sup>

In general, computational simulations based on periodic 210 211 DFT have a smaller computational cost than standard corre-212 lation methods. Therefore, an important step in the DFT 213 calculation is the choice of the functional to be used in the 214 simulation. Some functionals are able to predict the structure 215 but underestimate the band gap; conversely, other functionals, 216 which are able to accurately describe the band gap, tend often 217 to overestimate the structural parameters. There are several 218 comparative studies that examine the accuracy of the func-219 tionals in predicting the structural and electronic properties of 220 molecules and solids.<sup>15,27</sup> The general conclusion is that none of the available functionals are able to simultaneously describe 222 all electronic and structural properties of the studied systems. 223 The successful for describing properties in solid state when 224 these depended on accurate approximation on the band gap 225 and band structure. In particular, the band gap energy is 226 remarkable information that can bring the possible applications 227 of materials. In this work, the B3LYP,<sup>29</sup> HSE06,<sup>30,31</sup> PBE0,<sup>32</sup> 228 and PWGGA<sup>33</sup> functionals were used. B3LYP,<sup>29</sup> which is the 229 most popular hybrid functional that mixes HF, LDA, and GGA, 230 has shown good results when applied both to solid state and 231 study of molecules.

The HSE06<sup>30,31</sup> functional is an hybrid short-range corrected gas functional where the correlation and exchange parts are evalugat ated at the PBE level with 0.25 of HF exchange and a screening gas parameter of  $\omega = 0.11$  bohr<sup>-1</sup>.

The importance of including a certain percentage of exact HF exchange in order to better describe the effect of the and structure and dielectric properties has already been proved by Lacivita et al.<sup>15</sup> For this reason we have selected global and range-separated hybrid functionals to be compared with a pure gradientcorrected one.

As a first step, the optimizations of the lattice parameters 244 and internal coordinates of wurtzite ZnO were conducted to 245 minimize the total energy of the structure at experimental 246 parameters. The ZnO wurtzite belongs to the space group 247 *P63mc* with a Bravais lattice (a = 3.250 Å and c = 5.207 Å)<sup>34</sup> 248 and can be depicted as planes of tetrahedrally coordinated 249 oxygen and zinc atoms alternately stacked along the *c*-axis. 250 The parameters calculated with the B3LYP functional were 251 a = 3.274 Å, c = 5.250 Å, and u = 0.383, which were in good 252 agreement with the experimental values.

The structural parameters calculated with B3LYP were qualitatively analogous in the case of HSE06 and PBE0; on the other hand, the functional PWGGA overestimated the values of the structural parameters and internal parameter u.

From the bulk optimized parameters, the (0001) monolayer surface (periodic in the *x* and *y* directions) was built, and an optimization of the fractional coordinates was performed. Subsequently, the relaxed monolayer surface was wrapped in



Figure 1. Schematic figure of the single-walled nanotube construction.

a 1D cylindrical structure (Figure 1), and the diameter and 261 chirality of the system were defined by a vector (n,m) forming 262 armchair (n,n) and zigzag (n,0) nanotubes with n = 4, 6, 8, 10, 263 12, 24, 48, and 96, which correspond to diameters ranging from 264 6 to 174 Å, which presents the same number of atoms. 265

The topological analysis of  $\rho(r)$  was obtained with the 266 TOPOND program<sup>18</sup> incorporated in the CRYSTAL14 package. 267 TOPOND has the advantages to exploit the full periodic theory 268 of the former package so that it provides a new and re- 269 formulated version of chemical concepts at the same level of 270 accuracy for systems periodic in any dimension, i.e., bulk, surfaces, 271 and nanotubes. 272

The main instruments adopted in this work to analyze 273 atomic interactions in the framework of Bader analysis are 274 presented below; theoretical details can be found in works 275 specifically devoted to topological analysis.<sup>35,36</sup> We will strictly 276 focus on the determination and characterization of the so-called 277 bond critical points whose properties allow for a unambiguous 278 classification of chemical interactions. 279

A critical point (CP) in  $\rho(r)$  is a point where the gradient of 280 the density vanishes,  $\nabla \rho(r) = 0$ . Each CP can be classified in 281 terms of the eigenvalues,  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  of the Hessian matrix 282 of the second-derivatives of  $\rho(r)$  evaluated at the CP; con- 283 sequently, each CP can be labeled with two indices (r,s) where r 284 is the number of nonzero  $\lambda_{(i=1,3)}$  values and s is the difference 285 between positive and negative eigenvalues. Of peculiar interest 286 are the bond critical points (BCP) corresponding to (3,-1) in 287 terms of the (r,s) notation and indicating a saddle in the 288 electron density scalar field, with a local minimum along the 289 atom—atom direction and two maxima in the perpendicular 290 directions. 291

Several quantities can be evaluated at BCP such as the 292 Laplacian,  $\nabla^2 \rho(r)$ , the potential energy density, V(r), the 293 positive definite kinetic energy density, G(r), and the total 294 electronic energy density, H(r) = V(r) + G(r), in terms of 295 which the bond degree,  $H(r)/\rho(r)$ , is defined. Moreover, the 296 local formulation of the virial theorem establishes a fruitful 297 relationship between some of them: 298

$$\frac{1}{4}\nabla^2 \rho(r) = V(r) + 2G(r) = H(r) + G(r)$$
(1) 299

In terms of these descriptor, the nature of bond interactions can 300 be rationalized as follows:<sup>20</sup> (i) covalent bonds exhibits negative 301 Laplacian and H(r) and a V(r)/G(r) ratio larger than two as a 302 consequence of an excess of potential energy at the BCP; 303 (ii) transit bonds are associated with positive Laplacian, an 304 almost zero value of the bond degree and 1 < V(r)/G(r) < 2; 305 (iii) ionic, hydrogen bonds and van der Waals interactions 306

Table 1. Bond Length (Zn-O; Å) and Bond Angle (Zn-O-Zn; deg) of Armchair and Zigzag Nanotubes

armchair							zigzag					
		B3LYP	HSE06	PBE0	PWGGA			B3LYP	HSE06	PBE0	PWGGA	
(4,4)	$d_1$	1.89	1.88	1.88	1.94	(4,0)	$d_1$	1.86	1.84	1.84	1.91	
	$d_2$	1.87	1.86	1.86	1.93		$d_2$	1.90	1.89	1.89	1.94	
	$\alpha_1$	117.37	117.35	117.36	117.53		$\alpha_1$	105.18	105.14	105.13	105.44	
	$\alpha_2$	120.29	120.34	120.34	119.97		$\alpha_2$	120.72	120.74	120.75	120.55	
(6,6)	$d_1$	1.89	1.88	1.88	1.94	(6,0)	$d_1$	1.87	1.86	1.86	1.93	
	$d_2$	1.88	1.87	1.87	1.94		$d_2$	1.89	1.88	1.88	1.94	
	$\alpha_1$	118.83	118.81	118.81	118.89		$\alpha_1$	113.04	112.99	115.96	113.33	
	$\alpha_2$	120.09	120.14	120.14	119.76		$\alpha_2$	120.30	120.32	120.18	120.13	
(8,8)	$d_1$	1.89	1.88	1.88	1.94	(8,0)	$d_1$	1.88	1.87	1.87	1.94	
	$d_2$	1.89	1.87	1.87	1.94		$d_2$	1.89	1.88	1.88	1.94	
	$\alpha_1$	119.35	119.33	119.33	119.51		$\alpha_1$	113.04	115.97	117.39	116.33	
	$\alpha_2$	120.02	120.08	120.08	119.69		$\alpha_2$	120.30	120.18	120.18	119.98	
(10,10)	$d_1$	1.89	1.88	1.88	1.94	(10,0)	$d_1$	1.88	1.87	1.87	1.94	
	$d_2$	1.89	1.87	1.87	1.95		$d_2$	1.89	1.88	1.88	1.94	
	$\alpha_1$	119.59	119.57	119.57	119.76		$\alpha_1$	117.45	117.40	118.18	117.76	
	$\alpha_2$	119.99	120.05	120.05	119.66		$\alpha_2$	120.09	120.11	120.07	119.92	
(12,12)	$d_1$	1.89	1.88	1.88	1.94	(12,0)	$d_1$	1.89	1.87	1.87	1.94	
	$d_2$	1.89	1.88	1.88	1.95		$d_2$	1.89	1.88	1.88	1.94	
	$\alpha_1$	119.73	119.70	19.70	119.89		$\alpha_1$	118.23	118.19	118.18	118.55	
	$\alpha_2$	119.98	120.03	120.03	119.64		$\alpha_2$	120.05	120.07	120.07	119.88	
(24,24)	$d_1$	1.89	1.88	1.88	1.94	(24,0)	$d_1$	1.89	1.88	1.88	1.95	
	$d_2$	1.89	1.88	1.88	1.95		$d_2$	1.89	1.88	1.88	1.93	
	$\alpha_1$	119.95	119.93	119.93	120.12		$\alpha_1$	119.60	119.55	119.55	119.93	
	$\alpha_2$	119.95	120.00	120.00	119.61		$\alpha_2$	119.99	120.02	120.02	119.82	
(48,48)	$d_1$	1.89	1.88	1.88	1.94	(48,0)	$d_1$	1.89	1.88	1.88	1.95	
	$d_2$	1.89	1.88	1.88	1.95		$d_2$	1.89	1.88	1.88	1.93	
	$\alpha_1$	120.01	119.99	119.99	120.18		$\alpha_1$	119.95	119.90	119.89	120.28	
	$\alpha_2$	119.94	119.99	119.99	119.61		$\alpha_2$	119.97	120.00	120.00	119.81	
(96,96)	$d_1$	1.89	1.88	1.88	1.94	(96,0)	$d_1$	1.89	1.88	1.88	1.95	
	$d_2$	1.89	1.88	1.88	1.95		$d_2$	1.89	1.88	1.88	1.93	
	$\alpha_1$	120.03	120.00	120.00	120.19		$\alpha_1$	120.03	119.98	119.98	120.37	
	$\alpha_2$	119.94	119.99	119.99	119.60		$\alpha_2$	119.97	120.00	120.00	119.80	

307 show positive Laplacian and H(r) and a V(r)/G(r) ratio lower 308 than 1 due to the dominance of kinetic energy at the BPC. 309 Integration of the charge density over the atomic basins gives 310 further information such as atomic volume, Bader's atomic 311 charges, and the partition of the energy in atomic contributions. 312 In this work, CPs have been searched using the eigenvector-313 following approach<sup>36</sup> and the Morse relationship

$$\mathbf{n}_{3,-3} - \mathbf{n}_{3,-1} + \mathbf{n}_{3,+1} - \mathbf{n}_{3,+3} = 0$$
(2)

315 where **n** identify the number of CP has been verified *a posteriori* 316 and is fulfilled for all the structures.

### 317 **RESULTS AND DISCUSSION**

**Structural Properties.** The calculated Zn–O bond length and angle in armchair and zigzag SWZnONTs (Figure 1) are reported in Table 1. The calculated bond length was approximately 1.89 Å for B3LYP, HSE06, and PBE0 and 1.94 Å for PWGGA. The average Zn–O–Zn bond angle for all nanotubes was 119° for all functionals. These parameters are similar to those of the (0001) monolayer surface but different from the bond length and angle observed in ZnO bulk, which are equal to 1.99 Å and 108.26°, respectively. When the nanotube diamter increases, the structure approaches the monolayer surface. These results were also observed by other authors. Lacivita and showed that the bond length of the (50,50) nanotube was 1.8970 Å, while that of the monolayer was 1.8969 Å, in good 331 agreement with the results obtained in this work. Zhou and 332 co-workers<sup>37</sup> reported zigzag nanotubes with a structure very 333 similar to that obtained for the (0001) surface and comparable 334 to that of carbon nanotubes. Krainara et al.<sup>38</sup> analyzed the 335 structure of ZnS zigzag single-walled nanotubes; the structure 336 obtained after the optimization closely resembled that obtained 337 for the surface, excluding the lower smoothness. These works 338 are in good agreement with this study in relation to the results 339 obtained for nanotubes as well as bulk and surface. 340

The  $E_s$  values of the nanotubes were calculated with all func-  $_{341}$  tionals and are reported in Table 2. For both nanotube types, a  $_{342}$  decrease of  $E_s$  with the increase of the nanotube diameter could  $_{343}$  be observed (see Figure 2), showing a stabilization in (12,12)  $_{344}$  and (12,0) nanotubes. Nanotubes with a large diameter are  $_{345}$  formed easier than those with a small diameter. All functionals  $_{346}$  showed the same behavior.  $_{347}$ 

The  $E_{\rm s}$  values for zigzag nanotubes are slightly higher than 348 the values calculated for armchair nanotubes; the small 349 difference, only 0.01 eV/atom, may depend on the method- 350 ology or the error accumulation in the numerical calculation 351 process; both can be obtained experimentally, depending of the 352 experimental conditions. Xu and coauthors<sup>39</sup> synthesized two 353 types of ZnO nanotubes on a Si substrate; the present study 354 suggests that they were armchair and zigzag type nanotubes. 355 However, Wang et al.<sup>10</sup> performed a theoretical study on ZnO 356 Table 2. Energy Strain (E<sub>s</sub>; eV/Atom) and Band Gap Energy (E<sub>gap</sub>; eV) for Nanotubes, Bulk, and (0001) Monolayer Surface

	B3L	ХЪ	HSI	E06	PB	E0	PWGGA		
nanotube	Es	$E_{\rm gap}$	$E_{\rm s}$	$E_{\rm gap}$	$E_{\rm s}$	$E_{\rm gap}$	Es	$E_{\rm gap}$	
(4,4)	0.050	4.42	0.050	4.30	0.050	5.04	0.044	2.14	
(6,6)	0.021	4.50	0.021	4.37	0.021	5.10	0.018	2.19	
(8,8)	0.013	4.51	0.013	4.39	0.013	5.13	0.010	2.21	
(10,10)	0.009	4.52	0.009	4.40	0.009	5.14	0.007	2.22	
(12,12)	0.006	4.53	0.006	4.41	0.007	5.15	0.005	2.23	
(24,24)	0.002	4.54	0.002	4.42	0.002	5.16	0.000	2.23	
(48,48)	0.001	4.54	0.001	4.42	0.001	5.16	-0.001	2.24	
(96,96)	0.001	4.54	0.000	4.42	0.001	5.16	-0.001	2.24	
(4,0)	0.199	4.23	0.197	4.10	0.198	4.86	0.178	2.01	
(6,0)	0.074	4.39	0.073	4.26	0.074	5.01	0.065	2.13	
(8,0)	0.038	4.45	0.038	4.33	0.038	5.08	0.033	2.19	
(10,0)	0.024	4.49	0.023	4.36	0.024	5.11	0.020	2.21	
(12,0)	0.017	4.50	0.017	4.38	0.017	5.12	0.014	2.21	
(24,0)	0.005	4.54	0.005	4.41	0.005	5.15	0.003	2.23	
(48,0)	0.002	4.54	0.002	4.42	0.002	5.16	0.000	2.24	
(96,0)	0.001	4.54	0.001	4.42	0.001	5.16	-0.001	2.24	
bulk	3.21		2.99		3.6	69	1.06		
surface	4.56		4.42		5.1	.7	2.23		



Figure 2. Energy strain and energy gap as functions of the nanotube diameter: (a) armchair; (b) zigzag.

357 nanotubes, indicating that ZnO zigzag nanotubes were the most 358 stable, but only a slight difference between the  $E_s$  values of 359 armchair and zigzag nanotubes could be observed for nano-360 tubes with the same diameter.

**Electronic Properties.** Figure S1shows the band structure and the total and projected DOS of ZnO bulk for all functionals. The shape of the band structure and DOS are qualiat tatively similar at all levels of theory. Upon analysis of the calculated structural parameter, band gap energy, surface energy, 365 elastic constants, and piezoelectric constants, the functional 366 B3LYP showed the best results; thus, we chose to present the 367 results for this functional. For this reason, the discussion refers to 368 the B3LYP functional. 369

In bulk ZnO, the top of the valence band (VB), coincident 370 with the Fermi level energy (-5.47 eV), is located at the  $\Gamma$  371 point. The band gap is direct, 3.21 eV, in accordance with the 372 experimental optically measured gap and other theoretical 373 works. An analysis of the DOS of the bulk model, shown in 374 Figure S1b, indicates that the VB consists mainly of 2p levels of 375 O atoms, and the intense peak is due to 3d orbitals of Zn 376 atoms. The main contribution of the conduction band (CB) 377 comes from 4s4p levels of Zn atoms. The calculated band gap 378 for the PWGGA level is considerably lower than that predicted 379 experimentally and the values calculated with the B3LYP, HSE06, 380 and PBE0 functionals. This underestimation is expected, as 381 the exchange-correlation functionals within the GGA family are 382 known to fail in describing the semiconductor character of some 383 solids. However, the LDA and PBE functionals were previously 384 tested for bulk. The calculated band gap energy, 0.89 and 385 1.05 eV, with LDA and PBE, respectively, were underestimated. 386

The optimized (0001) monolayer surface also exhibited a  $_{387}$  direct band gap, 4.56 eV for B3LYP, at  $\Gamma$  point (Figure S2), and  $_{388}$  a similar contribution of the atomic orbital, with major contri-  $_{389}$  butions from oxygen at the VB and zinc at the CB.  $_{390}$ 

The results presented in Table 2 show the values of  $E_{gap}$  of 391 the nanotubes.  $E_{gap}$  increased from 4.42 to 4.54 eV for (4,4) 392 and (96,96), respectively, and from 4.23 to 4.53 eV for (4,0) 393 and (96,0), respectively. The HSE06 functional showed similar 394 values of  $E_{gap}$ , whereas PBE0 produced overestimated values 395 (see Table 2); PWGGA presented values well below those 396 obtained with the other functionals. 397

Figures 3 and 4 shows the band structure and DOS at B3LYP 398 level for three selected models of armchair ((6,6), (12,12), 399 and (24,24)) and zigzag ((6,0), (12,0), and (24,0)) nanotubes, 400 respectively. All nanotubes have a direct band gap at the  $\Gamma$  401 point, coincident with the observed direct bad gap for bulk and 402 (0001) monolayer surface. 403



Figure 3. Band structure and density of states of armchair nanotubes: (a, b) (6,6); (c, d) (12,12); (e, f) (24,24).

The band structures for models with larger diameters are 405 very similar and remain concentrated near the top and bottom 406 of the VB and CB, respectively. The DOS analysis showed a 407 major contribution of the  $2p_y$  and  $2p_z$  orbitals of oxygen atoms 408 in the top of the VB band and 3d orbitals of zinc atom in the 409 intermediate region of the VB. In the CB, the contributions of s 410 and p orbitals of zinc atoms were observed.

In general, the calculated band gaps of the nanotubes are greater than  $E_{gap}$  of the bulk and have a similar value to that of the (0001) monolayer surface. The band gap value converges to 414 4.54 eV.

The calculated Bader atomic charges for all nanotubes were 416 1.29 and -1.29 au for the zinc and oxygen atoms, respectively. 417 For comparison, the Mulliken charges analysis was conducted. 418 The calculated values for all models of armchair and zigzag 419 nanotubes were 88.3 and -88.3 au for zinc and oxygen atoms, 420 respectively. Both nanotubes present Bader and Mulliken 421 atomic charges very close to the (0001) monolayer surface. Notably, the values obtained for both population analyses 422 cannot be directly compared with respect to their magnitude 423 but can be compared for tendency. Indeed, there is not an 424 unique method to obtain the atomic charge on each atom, 425 which is dependent on the basis set and the method of calcu-426 lation. In particular, the Mulliken charges, which are not based 427 on density analyses, can be directly obtained from the corre-428 sponding wave function of that atom. However, this is not quite 429 accurate because of the overlapping of the wave functions of 430 neighboring atoms.

**Vibrational Properties.** The vibrational spectra of infrared 432 (IR) and Raman, and the corresponding modes, for bulk, 433 (0001) monolayer surface, (12,12), and (12,0) nanotubes, are 434 shown in Figures S3–S6; no shifts are made. 435

ZnO bulk presents two IR-active modes, located at  $_{436}$  389.34 cm<sup>-1</sup> (A, oxygen wagging) and 417.65 cm<sup>-1</sup> (E, oxygen  $_{437}$  scissoring), and four Raman-active modes, 104.92 cm<sup>-1</sup>  $_{438}$  (E, Zn–O twisting), 389.34 cm<sup>-1</sup> (A, oxygen wagging), 439

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Figure 4. Band structure and density of states of zigzag nanotubes: (a, b) (6,0); (c, d) (12,0); (e, f) (24,0).

440 417.65 cm<sup>-1</sup> (E, oxygen scissoring), and 441.90 cm<sup>-1</sup> (E, oxygen 441 twisting). For the (0001) monolayer surface, there are similar 442 assignment movements, both active in IR and Raman, located at 443 302.47 cm<sup>-1</sup> (A, oxygen wagging) and 555.41 cm<sup>-1</sup> (E, oxygen 444 scissoring).

<sup>445</sup> For the (12,12) nanotube, there are three IR-active modes, <sup>446</sup> 290.56 cm<sup>-1</sup> (E<sup>"</sup><sub>3</sub>, oxygen wagging), 558.86 cm<sup>-1</sup> (A'<sub>w</sub> oxygen <sup>447</sup> rocking), and 620.65 cm<sup>-1</sup> (E<sup>"</sup><sub>3</sub>, oxygen scissoring), and six <sup>448</sup> Raman-active modes, 90.71 cm<sup>-1</sup> (E'<sub>5</sub>, Zn–O stretching), <sup>449</sup> 278.72 cm<sup>-1</sup> (E'<sub>5</sub>, oxygen wagging), 301.27 cm<sup>-1</sup> (A'<sub>g</sub> oxygen <sup>450</sup> wagging), 559.96 cm<sup>-1</sup> (E"<sub>3</sub>, Zn–O stretching), 562.31 cm<sup>-1</sup> <sup>451</sup> (A'<sub>g</sub>, oxygen rocking), and 650.54 cm<sup>-1</sup> (E'<sub>5</sub>, oxygen <sup>452</sup> scissoring). No corresponding modes of IR and Raman were <sup>453</sup> observed.

<sup>454</sup> The (12,0) nanotube present  $2A_1 + 2E_5$  IR and Raman-<sup>455</sup> active modes, 282.63 cm<sup>-1</sup> ( $E_5$ , oxygen wagging), 527.24 cm<sup>-1</sup> <sup>456</sup> ( $A_1$ , oxygen rocking), 576.27 cm<sup>-1</sup> ( $A_1$ , oxygen wagging) and <sup>457</sup> 640.17 cm<sup>-1</sup> ( $E_5$ , oxygen scissoring), and  $E_5 + E_{10}$  only Raman active, 28.46 cm  $^{-1}$  (E  $_{5}$  O rocking), 144.90 cm  $^{-1}$  (E  $_{10}$  Zn–O  $_{458}$  stretching).

There are no similar assignment movements for armchair 460 and zigzag nanotubes. The modes of both SWZnONT do not 461 have any direct correspondence in the vibrational spectrum of 462 the (0001) monolayer surface and bulk. 463

The Raman and IR data can be used to provide a fingerprint 464 by which the chirality of nanotubes can be indentified in experi-465 mental research. 466

**Topological Analysis.** The topological analysis of the elec- 467 tron density (Table 3), in particular as regards the properties of 468  $\rho(\mathbf{r})$  at the BCP, can provide important information on 469 chemical bonds, fundamental to understand the type of inter- 470 action between two atoms and the modification induced by 471 structure rearrangements.

The main effects on charge topology and Zn-O interaction  $_{473}$  emerge as the surface is formed and are strictly related to the  $_{474}$  decrease in the coordination sphere of both the atoms.  $_{475}$ 

Table 3. Several Properties (Electron Charge Density, Its Laplacian, the V/G Ratio, and the Bond Degree  $H/\rho(r)$ , and Ellipticity, All in Atomic Units) Computed at the Zn–O Bond Critical Point in Different Structures at the B3LYP Level<sup>4</sup>

	topological properties									charges			
		$d_{ m F}$	SCP					Mulliken		Bader		Bader	
	$d_1$	Zn	0	$\rho(r)$	$\nabla^2 \rho$	V/G	$H/\rho(r)$	ε	Zn	0	Zn	0	O (%)
bulk	1.99	0.96	1.04	0.08	0.41	1.06	-0.08	0	0.914	-0.914	1.30	-1.30	57
surface	1.89	0.92	0.97	0.10	0.59	1.06	-0.09	0.029	0.884	-0.884	1.27	-1.27	55
(24,24)	1.89	0.92	0.97	0.10	0.59	1.06	-0.09	0.029	0.885	-0.885	1.27	-1.27	55
(24,0)	1.89	0.92	0.97	0.10	0.59	1.06	-0.10	0.029	0.885	-0.885	1.27	-1.27	55
(4,4)	1.87	0.91	0.95	0.10	0.63	1.06	-0.10	0.027	0.883	-0.883	1.27	-1.27	55
	1.89	0.92	0.97	0.10	0.58	1.06	-0.09	0.029					
(4,0)	1.86	0.91	0.95	0.11	0.66	1.07	-0.11	0.018	0.883	-0.883	1.27	-1.27	54
	1.90	0.92	0.98	0.10	0.57	1.06	-0.10	0.032					

"Bond distances as well as Mulliken and Bader charges are reported for sake of comparison; distances are in angstroms. The percentage of oxygen volume, as evaluated by the integration of the charge over the atomic basin, with respect to the total Zn plus O is also given.



Figure 5. Laplacian of the electron density in the plane containing the oxygen atoms evaluated at the B3LYP level. (a) ZnO monolayer, (b) armchair (24,24), (c) (4,4) and (d) zigzag (24,0), (e) (4,0). A logarithmic scale is adopted between -8.0 and 8.0 au. Continuous red and dotted blue lines indicate positive and negative contour levels, respectively.

476 Although the significant structural deformation, it seems that 477 bond framework and charge density are not very much 478 perturbed. As surface occurs, the Zn–O distance is shortened, 479 the charge is slightly less polarized between the two atoms, and 480 the volume of the anion is sensitively reduced with respect to 481 that of Zn. By the point of view of main topological properties 482 (24,24) and (24,0) tubes are almost indistinguishable from the 483 monolayer, and this can also be seen looking at Figure 5 where <sup>484</sup> the values of the Laplacian,  $\nabla^2 \rho$ , in the plane containing the 485 oxygen atoms are plotted and compared with the surface ones. 486 In these case, regions of charge depletion and concentration are 487 equally presented and electronic distribution seems not affected 488 by the finite dimension of the (24,24) and (24,0) surface. The 489 few deformations appearing in (4,4) and (4,0) Laplacian only 490 involve the valence region of the shell structure of the atoms 491 closest to the border but do not change significantly the Zn–O 492 bond nature.

<sup>493</sup> Indeed, topological indicators support for all the systems <sup>494</sup> the general description of the ZnO bond as belonging to the transit region, so neither ionic nor covalent. BCPs are almost  $_{495}$  equidistant from the two nuclear attractors, and negative bond  $_{496}$  degrees, although small in absolute values, indicate a local  $_{497}$  excess of potential energy, as for covalent bonds; also the  $_{498}$  very small values of ellipticity,  $\varepsilon$ , highlight the cylindrically  $_{499}$  symmetric shape of the bonds and their poor directionality. On  $_{500}$  the other hand, BCP densities around 0.1 e/bohr<sup>3</sup> and positive  $_{501}$  values of the Laplacian suggest a ionic nature of the Zn–O  $_{502}$  bond.

Interesting enough, in the smaller nanotubes, (4,4) and (4,0),  $_{504}$  the two Zn–O bonds that according to Table 1 have different  $_{505}$  length exhibit sensitive differences in the topology, in particular  $_{506}$  as regards Laplacian and ellipticity.  $_{507}$ 

Finally, Bader approach represents structures where the 508 lowering in the dimensionality (passing from bulk to surfaces) 509 is accomplished with a decreasing of the atomic charge whereas 510 Mulliken analysis lands at an opposite description, as already 511 stated in the Electronic Properties section. 512

### 513 CONCLUSION

514 Periodic DFT calculations with B3LYP, HSE06, PDE0, and 515 PWGGA functionals and all-electron Gaussian basis set were 516 performed to simulate the structural and electronic properties 517 of armchair and zigzag SWZnONTs with different diameters.

518 The results obtained with B3LYP and HSE06 presents 519 similar values of bond length, bond angle,  $E_{s}$ , and  $E_{gap}$ ; however, 520 PWGGA functional overestimated all mentioned parameters 521 cited above.

The calculated  $E_s$  values of nanotubes with all functionals s23 showed a decrease behavior with the increase of the nanotube s24 diameter; however, the  $E_s$  stabilizes in (12,12) and (12,0) nanos25 tubes, concluding that large diameter nanotubes are formed s26 easier than those with a small diameter.

<sup>527</sup> The calculated  $E_{\rm gap}$  of the SWZnONT are greater than  $E_{\rm gap}$  of <sup>528</sup> the bulk and have a similar value to (0001) monolayer surface. <sup>529</sup> The  $E_{\rm gap}$  values of nanotubes converge to 4.54 eV, maintaining <sup>530</sup> the semiconductor character.

The band structures for models with larger diameters are siz very similar and remain concentrated near the top and bottom siz of the VB and CB, respectively. The DOS analysis showed a siz major contribution of the  $2p_y$  and  $2p_z$  orbitals of oxygen atoms sis in the top of the VB band, and 3d orbitals of zinc atom in the sid intermediate region of the VB. In the CB, the contributions of s siz and p orbitals of zinc atoms were observed.

The bulk and (0001) monolayer surface presents two similar sag assignment movements, both active in IR and Raman. However, there are no similar assignment movements for armchair s41 and zigzag nanotubes, and the modes of both SWZnONT do s42 not have any direct correspondence in the vibrational spectrum s43 of the (0001) monolayer surface and bulk.

544 Zn–O bond length and bond angle, Mulliken and Bader 545 charges, and all topological descriptors of ZnO interaction 546 nanotubes of both chirality are similar to the same quantities as 547 computed for the (0001) monolayer surface.

548 Owing to these analyses, both chiralities with large diameter 549 can be used interchangeably in semiconductor applications. 550 These theoretical models can be extended and applied to other 551 computational simulations, as doping or adsorption process.

### 552 ASSOCIATED CONTENT

### **S53 Supporting Information**

554 The Supporting Information is available free of charge on the 555 ACS Publications website at DOI: 10.1021/acs.jpcc.5b11905.

Band structure and density of states of ZnO bulk and
 monolayer surface (0001); vibrational IR and Raman
 spectra (PDF)

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562 **Notes** 

563 The authors declare no competing financial interest.

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