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Ab initio structure modeling of ZrO_2 nanosheets and single-wall nanotubes

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ABSTRACT

We employed first-principles simulations using hybrid exchange–correlation density functional PBE0 within LCAO approximation to investigate the properties of ZrO_2 nanotubes constructed from the different zirconia polymorphs, in an attempt to understand the relation between the bulk zirconia atomic structure and the stability of zirconia nanotubes. For the rolling of nanotubes we used the relaxed or reconstructed thin slabs obtained by cleaving cubic, tetragonal and monoclinic zirconia parallel to all possible low-index faces. The structure of nanotubes has been optimized with respect to unit cell constant and intracell degrees of freedom consistent with the initial rotohelical symmetry. The calculated nanotube formation and strain energies show that the most stable tubes with thin (one ZrO_2 layer) walls originated from the hexagonal (1 1 1) nanosheets of the cubic fluorite phase. The tubes with walls composed of two ZrO_2 layers, most likely have lepidocrocite morphology. The tubes with thicker walls can possess a different structure originating from cubic, tetragonal or orthorhombic phases. The comparison of similar zirconia and titania nanotubes provides evidence that zirconia nanotubes are more stable relative to the precursor nanosheets, while titania nanotubes are more stable relative to the parent bulk phases.

1. Introduction

During the past decade great progress has been achieved on the synthesis and study of various nanostructure materials containing zirconia. Significant attention has been paid to ZrO_2 nanotubes (ZNTs) because of their existing and potential applications, such as host matrix for optical functional materials, components of oxygen sensors, and electrolytes in solid-oxide fuel cells [1–4]. The bioactivity of zirconia nanotubes at different annealing temperatures was investigated to provide their future use for the medical purposes [2,5]. Zirconia has also been reported [6] as one of the most suitable dopants to enhance the thermal stability and activity of TiO_2 nanomaterials.

In recent years, zirconia nanotubes have been successfully prepared by various methods such as template-assistant depositions, hydrothermal treatments, and direct anodization methods [3,4].

Rao et al. [7] synthesized zirconia nanotubes using multi-walled carbon NTs as templates. The obtained nanotube outer diameters were 40 nm, and the wall thicknesses were 6 nm. The atomic structure of the obtained NTs was an equal mixture of tetragonal and monoclinic crystalline phases. Gundiah et al. [8] fabricated zirconia nanotubes using a template-based synthesis. The obtained nanotube outer diameters were approximately 25 nm, the inner diameters were approximately 4–7 nm, and the lengths were several hundred nm. The crystal structure was the mixed phase of monoclinic, cubic, and tetragonal. Shin and co-authors [9,10] synthesized zirconia nanotubes using a porous polycarbonate membrane as a template. The electron diffraction pattern shows that the crystalline structure of ZNTs corresponds to a tetragonal polymorph. The authors concluded that tetragonal zirconia nanotubes may exist at room temperature without any stabilizers because of the increased stress at the curved NT surfaces.

High aspect ratio zirconia nanotubes with a diameter of 50 nm have been obtained by Tsuchiya et al. [11] via the electrochemical anodization of zirconium. X-ray diffraction (XRD) investigation reveals that the nanotubes have a cubic crystalline structure directly after anodization without any further annealing. Hahn et al. [12] reported self-organized nanotubular layers of ZrO_2 which were electrochemically grown by tailored anodization in an aqueous electrolyte. The atomic structure of the samples was determined by XRD measurements, which clearly demonstrated the presence of cubic crystalline phase.

The zirconia nanotube arrays with a diameter of about 130 nm, a length of up to 190 μm and aspect ratios of more than 1400 were prepared by anodizing a zirconium foil [5,13]. The as-prepared nanotube arrays consist of amorphous zirconia. Monoclinic and tetragonal zirconia coexisted when NTs were annealed at 400 °C and 600 °C while monoclinic zirconia was obtained at 800 °C. Zirconia nanotubes with a diameter of up to 40 nm and a length of up to 12 μm were prepared [14] using the direct anodization method. Further analysis shows that the crystalline phases of the obtained structure were predominantly orthorhombic phase (the space group was not specified) with some monoclinic phase admixture.

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A brief review presented above shows that ZNTs can have a different morphology depending on method and conditions of their fabrication. It follows from the reported data that the experimental studies cannot provide the detailed description of the equilibrium atomic-level morphology of zirconia nanotubes. A similar situation takes place for the titania nanotubes (TNTs). However, the recent computer simulations permit to establish the most probable structures of single- [15–20] and double-walled [21] TNT and to estimate their relative stability. At the same time, the theoretical studies of ZNTs are presently lacking. In this work, we employ the first-principles calculations in an attempt to understand the relation between the bulk zirconia atomic structure and the stability of ZNT folded from the nanosheets corresponding to the different faces of various ZrO_2 polymorphs. To this purpose, the structural and surface properties of thin slabs cleaved from zirconia bulk phases have been carefully studied. Finally, the results of calculations of the zirconia single-wall nanotubes are presented for the first time, and their properties and symmetry are discussed.

2. Computational details

To perform first-principles calculations we used the CRYSTAL09 computer code [22,23]. This code employs the Gaussian-type functions localized at atoms as the basis set for an expansion of the crystalline orbitals. Due to the use of a localized atomic basis the CRYSTAL09 code allows us to treat 2D- and 1D-periodical systems without introducing an artificial 3D periodicity, necessary in plane wave calculations. Our computations were performed using a hybrid exchange–correlation functional PBE0 [24,25] involving a mixture of non-local Fock exact exchange and PBE [26] exchange–correlation part. This parameter-free exchange–correlation functional PBE0 is established from the perturbation theory. It well reproduces the properties of many strongly correlated systems [27] and was successfully applied to various oxide systems [28].

The CRENBL effective core pseudopotential was adopted for the Zr atom [29]. We used the small-core pseudopotential, which replaces only inner core electrons, whereas the sub-valence electrons (4*s* and 4*p* in our case), as well as valence electrons, are calculated self-consistently. To prevent the quasi-linear dependences, the diffuse exponents less than 0.1 a.u. were removed from the original [29] basis and the exponents of other polarization functions have been reoptimized for the periodic calculations. Oxygen atoms were treated with an all-electron basis [30]. The reciprocal space integration was performed by sampling the Brillouin zone of the cubic crystal with a $12 \times 12 \times 12$ Monkhorst–Pack mesh [31], which was reduced inversely to the cell constants in other periodical systems to provide approximately uniform **k**-point spacing.

We employed the built-in capabilities of the CRYSTAL09 code and the Surface Builder module of the Materials Studio software package [32] for preparing the initial structure of nanosystems and for symmetry analysis. The lattice parameters and fractional positions of all atoms in the considered systems were fully optimized. Ionic and cell relaxations were performed until the root-mean-square forces on the atoms were less than 0.003 eV/Å in bulk and slab systems, and less than 0.03 eV/Å in the nanotubes.

3. Results and discussion

3.1. Properties of ZrO_2 polymorphs

The prototype bulk crystal structure is one of the main factors that influence the properties of nano-sized systems. Zirconia is an oxide which exhibits a large variety of polymorphs. The properties of bulk ZrO_2 are well studied experimentally [33] and theoretically [34–41]. It was established that ZrO_2 has three zero-pressure modifications. At high temperatures ($t > 2350$ °C), zirconia adopts a cubic fluorite structure ($Fm\bar{3}m$), while at low temperatures ($t < 1150$ °C), a monoclinic baddeleyite ($P2_1/c$) structure is preferred [42], thus representing a ground state of zirconia. A tetragonal phase exists at intermediate temperatures; it can be viewed as a simple perturbation of the cubic phase in which the oxygen atoms are displaced alternately along the 4_2 axis by ±0.2 Å, resulting in a $P4_2/nmc$ symmetry.

Besides the well-known monoclinic, tetragonal, and cubic phases, two orthorhombic high pressure phases with space group symmetry *Pbca* (orthorhombic-I) and *Pnma* (orthorhombic-II) are stable above 3 and 20 GPa, respectively [43,44]. The dense orthorhombic-II phase (isostructural with cotunnite) is of particular interest because it can be quenched to ambient conditions [44].

The relative stability of ZrO_2 phases can be influenced by the crystallite size. It is well known that small zirconia particles suspended in a host matrix do not transform from tetragonal to monoclinic, even well below the bulk transition temperature unless subjected to an external stress field or heating above 700 K [45,46]. Moreover, Wang et al. [47] have found that tetragonal zirconia can be obtained in particles with sizes below 40 nm at room temperature. Structure studies [48] of ZrO_2 deposition on the amorphous silica have shown that the thin ZrO_2 film growth starting from the formation of amorphous phase proceeds with preferential growth of crystallites of tetragonal and cubic structures in the direction [001]. The structure analysis of the fabricated ZNT also gives evidence that the small particle size may stabilize the virtually unstable phases. This means that ZNT can possess cubic, tetragonal or orthorhombic morphology. It also should be noted that the additional tetragonal, orthorhombic, and hexagonal phases of ZrO_2 have also been reported at high pressures and/or high temperatures [43,49,50].

In this work we primarily consider the thin sheets generated from cubic, tetragonal and monoclinic phases as the precursors for nanotubes. Therefore, we start our study with calculations of the structure and properties of the corresponding bulk crystals. At the same time, these crystals play a role of benchmark systems for testing the applicability of the accepted computation method. Further, during the calculations of nanolayers we found that one of the considered sheets (see the next subsection) has been reconstructed to a cotunnite-type layer. Because of this, we have appended the high-pressure orthorhombic-II phase to the set of three low-pressure phases. For similar reasons, we have calculated the rutile-like hypothetical phase of ZrO_2. The hypothetical anatase-like phase of ZrO_2 has been studied primarily because of the prospective comparison with TiO_2 nanotubes.

In Table 1 we compare the calculated properties of four ZrO_2 phases with the experimental data. As it follows from Table 1, the theoretical structure parameters differ from the experimental estimations by 1% or less. The reported values are of better quality than those obtained in other works [36,40] using Generalized Gradient Approximation (GGA). Our calculations reproduce the cohesion and relative energies of the different phases as well. The bulk moduli values have been obtained via Birch–Murnaghan third-order equation of state, and they are in agreement with both the experimental and theoretical results. In Table 1 we also report the values of the band gap, which, as expected, are much better reproduced using the hybrid exchange–correlation functional compared to plain GGA.

3.2. Structure and stability of ZrO_2 nanosheets

The thin sheets of zirconia exhibit a variety of structures because of the existence of several crystalline bulk polymorphs. We consistently considered cubic, tetragonal, and monoclinic faces with the different (low) crystallographic indexes. The hypothetical