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Density functional theory study of structure and bonding of water on alumina nanotube

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ABSTRACT

Geometry and electronic structure of alumina nanotubes (ANT) were studied using hybrid B3LYP density functional method. Three models of finite length nanotubes, including nanotube with closed ends (CEANT), nanotube with one opened end (OOEANT) and nanotube with two opened ends (TOEANT) were considered. The calculated density of states and natural atomic orbitals analysis predict that HOMO and LUMO of nanotubes arise mostly from O *2p* and Al *3s* atomic orbitals, respectively. For CEANT and OOEANT, the electron density of HOMO concentrates over the center of nanotube, while the LUMO distributes over the end caps. HOMO and LUMO of TOEANT localize at the center of nanotube. The adsorption strength of the active sites of alumina nanotube (OOEANT) was evaluated using the interaction with water molecule. The relative strength of alumina nanotube adsorption sites was predicted as opened end > closed end (end cap) > hemisphere cap > center of nanotube using CAM-B3LYP method.

1. Introduction

Inorganic fullerenes and nanotubes are an important group of nanostructures, which have broad applications such as energy storage, sensing devices, medicine, drug delivery, gas storage and catalysis [1–5]. Recently, very interesting theoretical studies on this field have been reported in the literature [6–15]. Moreover, the experimental findings about these compounds have been reviewed by several research groups [1–5,16–22].

Amongst the inorganic nanostructures, the Al_2O_3 materials are very attractive since their thermal, chemical, and mechanical stability. These materials are widely used as industrial catalysts, catalyst supports, ion exchangers and adsorbents [23]. Recently, attention has been paid to synthesis and characterization of alumina nanoparticles [24], nanocapsules [25], nanowires [26], nanotrees [27], nanorods [28,29], nanochannels [30] and nanotubes [31–44]. These nanostructures are similar in composition but different in shape. Structure determination of these compounds by experiment methods is often extremely difficult; but theoretical studies have played important role in investigating the structure and electronic properties. For example, qualitative quantum chemical calculations predicted some structural models for γ-alumina including defect spinel, nonspinel and hydrogenated spinel [45–53]. Sohlberg et al. suggested the presence of various amounts of hydrogen within the bulk structure of spinel γ-alumina [45]. Wolverton and Hass indicated that hydrogen spinel is thermodynamically unstable with respect to decomposition into an anhydrous defect spinel plus boehmite [46]. Raybaud and coworkers presented a complete nonspinel structure based on molecular dynamic simulations and density functional theory (DFT) calculations of the dehydration of boehmite [47,48]. Paglia et al. reported that a nonspinel structure matches data obtained by neutron diffraction experiments [49,50]. Sun et al. using the simulated XRD calculations predicted that the spinel related structure model is better than the nonspinel model could describe the bulk structure of γ-Al_2O_3 [51]. Ferreira et al. discovered that the spinel model is thermodynamically more stable and the infrared spectrum complement the experimental data [52]. The refined occupancy parameters obtained for a single crystal X-ray of γ-Al_2O_3 show that, in addition to the ideal spinel positions, approximately 6% of Al ions also occupy nonspinel positions [53].

Recently, Linnolahti and Pakkanen proposed models for alumina nanoballs based on the threefold coordinated nature of aluminum atoms [54]. Charkin et al. [55], Dabbagh et al. [56], and Zheng et al. [57,58] applied these models to calculate complexation with NH_3, substitutional doping with B, Ga and In atoms, and modification with transition metal atoms (Co, Ni and Mo), respectively. Sun et al. studied the structure and the stability of $(Al_2O_3)_n$ clusters (n = 1–10 and 30), and their practical application for hydrogen adsorption [59]. They found global energy minimum for sizes n = 1–5 as perfect cages. For larger clusters, the cage-dimer and then for the size of n = 10 an onion-like structure is more favorable [59]. The small $(Al_2O_3)_n$ clusters (n = 1–5) were also studied by Woodley [60]. The Boltzmann (room temperature)-weighted superposition of spectra for the low-energy local minimum

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$(Al_2O_3)_4$ was found to be similar to the experimental data taken from the X-ray photoelectron spectrum and the ultraviolet photoelectron spectrum for bulk alumina [60]. Rahane et al. studied the atomic structures, growth behavior, vibrational and electronic properties of $(Al_2O_3)_n$ clusters ($n = 1–10$) [61]. The best performance was obtained for 4- and 6-membered rings isomers with lowest energy [61]. Li and Cheng obtained the geometrical structures of $(Al_2O_3)_n$ clusters ($n = 1–7$) via genetic algorithm and density functional theory [62]. The stability and bonding properties of single-cage and core–shell cage $(Al_2O_3)_n$ clusters ($n \leqslant 30$) were studied by Gu and co-workers [63]. The core–shell clusters are found to be more stable than the corresponding single-cage clusters and predominate in the medium-sized clusters [63]. The rapidly developing area of computational modeling of oxide materials at the nanoscale has been reviewed by Bromley et al. [64,65].

Alumina nanotubes were prepared successfully via various electrochemical and hydrothermal conditions [31–44]. Bao et al. [31–33] and Mei et al. [34] reported the synthesis of ANT by employing the electrochemical etching of Si-based Al films using anodizing method of Si-based aluminum membrane. Lee et al. [35] reported a continuous process for structurally well-defined ANT based on pulse anodization of aluminum. Xiao et al. [36] produced ANT by etching porous alumina membranes. Hwang et al. [37] reported the formation of ANT by wet-etching ZnO core nanowires in the ZnO/Al_2O_3 core/shell nanofibers. Lee et al. [38] fabricated ANT by coating and filling the multi walled carbon nanotubes with atomic-layer deposition. Other research groups have reported the synthesis of ANT from polymer composite materials, or using carbon nanotubes and nano fibers as templates [39–41]. The synthesis of ANT was reported by Fontes Diniz et al. using hydrolysis of aluminum isopropoxide followed by gelation and drying under hydrothermal condition [42]. Qu et al. [43] and Lu et al. [44] obtained the Al_2O_3 nanotubes by similar approach and using anionic surfactants as a template. Large number of studies on the synthesis and characterization of alumina nanotubes have been reported in the literature. However, limited computational analysis has been done on the structure and catalytic property of these materials. Theoretical studying of alumina nanotubes in the literature is limited to the publication of Linnolahti and Pakkanen. They reported the structure and relative stability of alumina nanotubes with closed ends [54]. There are reports on AlO(OH) (hydroxyalumina) [66], $Al(OH)_3$ (aluminum hydroxide) [67] and Al_2O_3–CNT (alumina-carbon nanotube) [68–70].

In the present study, the electronic property and structure of opened end alumina nanotubes (ANT with one opened end (OOEANT) and two opened ends (TOEANT)), in comparison to alumina nanotubes with closed ends (CEANT) were investigated using B3LYP level of theory. To evaluate the active site of alumina

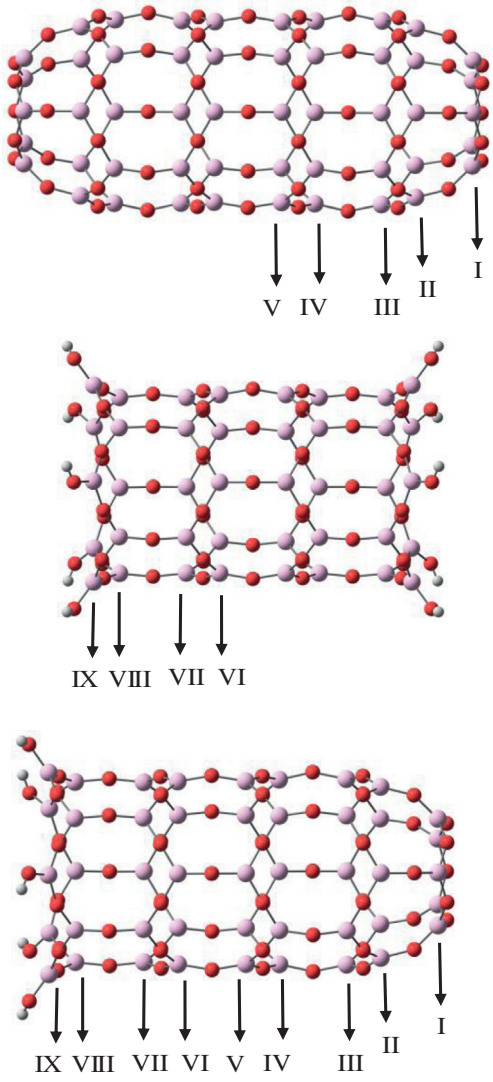

Fig. 1. The optimized geometry of alumina nanotubes calculated by B3LYP/6-31++G**/LanL2DZ level of theory.

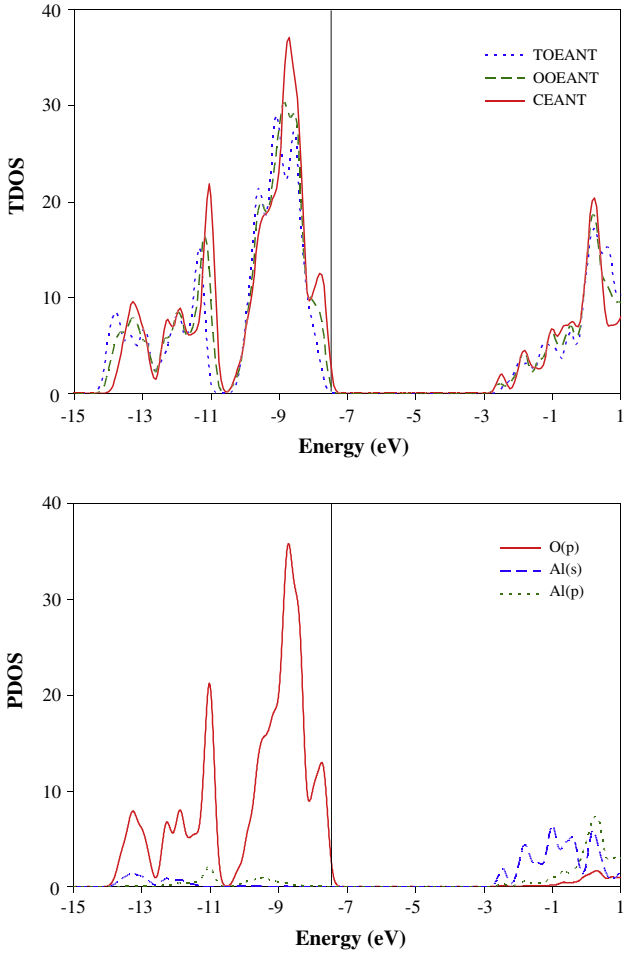

Fig. 2. Top: total density of states (TDOS) of various structural models of alumina nanotubes (CEANT, OOEANT and TOEANT) calculated by B3LYP/6-31++G**/LanL2DZ level of theory. Bottom: partially density of states (PDOS) of CEANT. The position of Fermi level is −7.5 eV.