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Theoretical characterization of layered silica nanostructures from first-principles prediction

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ABSTRACT

Using first-principles calculations, we study the structural, mechanical and electronic properties of the layered silica nanostructures built on base of silica bilayers consisting of four- and six-membered Si–O ring (4 MR and 6 MR) units. These silica nanostructures have high stability and good flexibility comparable to graphene and can serve as a promising precursor for the fabrication of well-ordered silica nanotubes. The porous structure and wide band gap of the silica nanomaterials may find applications in gas separation, slow-release microcapsules, and catalyst supports.

1. Introduction

Silica nanostructures have been the focus of much research, due to their potential applications in biocatalysis, bioseparation [1,2], nanoscale electronic devices [3,4], nanoscale reactors [5,6] and protection of environmentally sensitive species [7,8]. Diverse forms of low-dimensional silica nanostructures with chain, ring, cage and tubular configurations have been proposed theoretically [8–17]. In contrast to bulk materials, these silica nanostructures always consist of two-, three-, four- and six-membered Si–O rings (2 MRs, 3 MRs, 4 MRs, 6 MRs) accompanied by the presence of non-bridging oxygen atoms (NBOs) [9–20]. Generally, small-membered n MR ($n \leq 6$) Si–O units have high intrinsic strain energy which is energetically disadvantageous. However, in order to reduce the number of dangling bonds, small membered Si–O rings and NBOs are inevitable in silica nanostructures. Therefore, their energetic stability is mainly dominated by the ratio of NBOs and the size of Si–O rings. Theoretical studies on silica nanostructures offer great opportunities for the experimental works that are seeking to realize them and provide vital information for understanding the growth mechanisms of silica nanomaterials.

Among these nanostructures, layered and tubular configurations are of particular interest and have drawn considerable attention both theoretically and experimentally. The layered structure of silicon is unstable due to the high preference of sp^3-hybridization of Si atoms, but the incorporation of O atoms can improve the stability making layered nanosheets and nanotubes possible [21]. Silica nanosheets (NSs) and nanotubes (NTs) composed of 3 MRs, 4 MRs and 2–6 MRs have been proposed on the basis of first-principles [17–27]. However, the intrinsic strain energy involved in these NSs and NTs due to the presence of small-membered Si–O rings remains very high, and that may be the reason why they have not yet been synthesized. Therefore, searching for novel silica NSs and NTs with lower strain energy is desirable.

Experimentally, an ultrathin silica film consisting of a two-dimensional (2D) network of a corner-sharing SiO_4 tetrahedron has been grown on a Mo(112) surface [28–36]. One oxygen atom (O') of each SiO_4 tetrahedral binds to the protruding Mo atoms of the Mo surface, while other oxygen atoms (O) are connected with two Si atoms in the 6 MRs, as shown in Fig. 1a. The silica layer has no dangling bonds. It is consistent with early experiments results. No dangling bonds can make the surface more stable [27]. More interestingly, the arrangement of Si atoms in this silica monolayer exhibits graphene-like features. A silica bilayer composing of two silica monolayers joined together by Si–O–Si linkages, as shown in Fig. 1a, has been proposed in previous literature [20] and realized experimentally [28–37]. This silica bilayer is made up of 6 MRs (in-plane) and 4 MRs (interlayer) with each atom being fully coordinated. Both 2 MRs and NBOs are excluded and lower strain energy can therefore be expected compared to other silica NSs involving small Si–O rings and NBOs.

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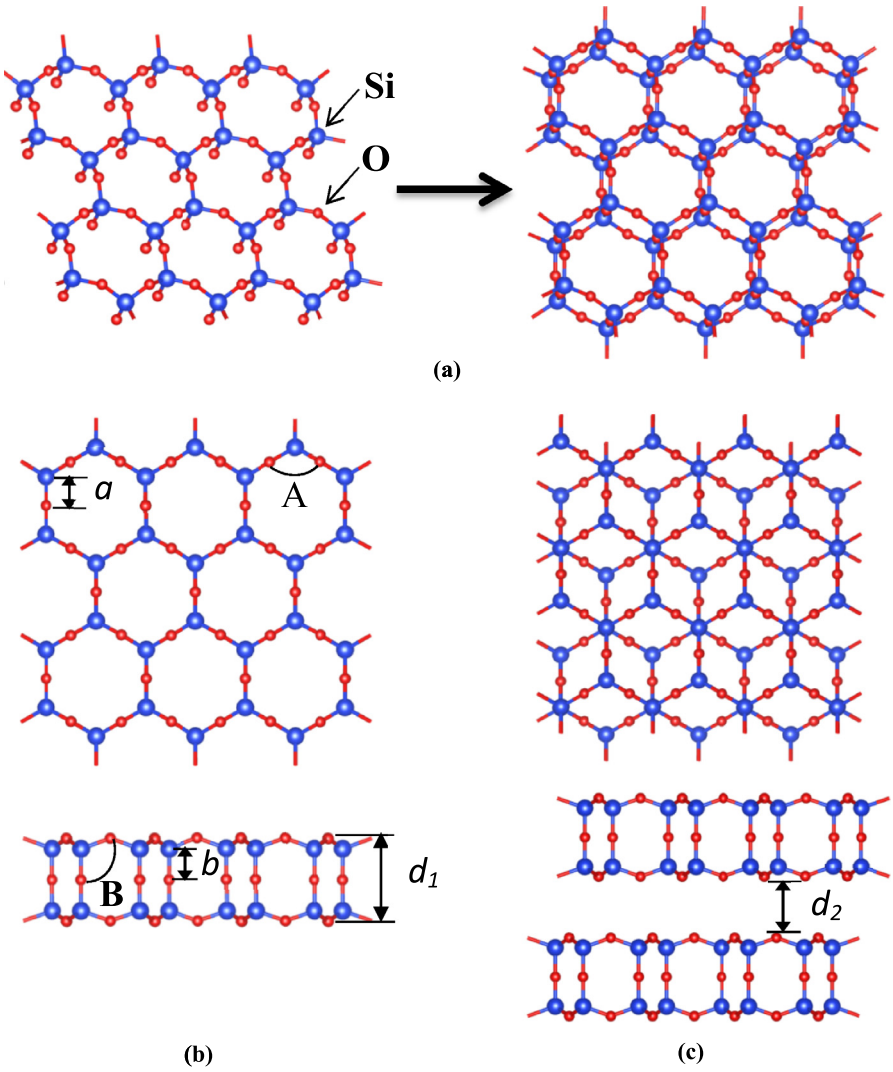

Fig. 1. (a) Schematic representation of the formation of silica bilayer from silica film grown on Mo substrate. Top- and side-views of silica NSs consisting of (b) one bilayer; (c) two silica bilayers.

In this contribution, we investigate the structural, energetic, mechanical and electronic properties of the silica bilayer and the layered nanostructures formed on the base of the silica bilayers from first-principles. We show that the silica bilayer and the related nanostructures have high stability and good flexibility comparable to graphene. Silica bilayer can serve as promising precursor for the fabrication of well-ordered silica nanotubes. The porous structure and wide band gap of the silica nanostructures may find applications in gas separation, slow-release microcapsules, and catalyst supports.

2. Methods and computational details

Our first-principles calculations were performed in the framework of density-functional theory (DFT) which is implemented in the Vienna ab initio simulation package known as VASP [38]. The electron–electron interactions were treated within a generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) for the exchange-correlation functional [39]. The van der Waals (vdW) correction (DFT-D2) proposed by Grimme [40,41] within the PBE functional was also included to deal with the vdW interactions between silica bilayers. The energy cutoff employed for plane-wave expansion of electron wavefunctions of both Si and O atoms were set to 500 eV. The Brillouin zone (BZ) integration was sampled on a grid of $8 \times 8 \times 1$ k-points for structural optimizations and $16 \times 16 \times 1$ k-points for electronic structure calculations. The supercells containing 12 atoms are repeated periodically along x- and y-directions while a vacuum region of about 15 Å was applied along the z-direction to avoid mirror interactions between adjacent images. Structural optimizations were carried out using a conjugate gradient (CG) method until the remanent force on each atom is less than 0.0001 eV/Å. The phonon spectra were calculated using a Fropho package on the basis of the dynamics matrices obtained from VASP calculations. This scheme can reproduce well the experimental data of the structural parameters of bulk α-quartz [42].

3. Results and discussion

We adopted the relative energy (E_R) of the silica nanostructures with respect to that of α-quartz to evaluate the energetic stability. We first considered the silica NSs consisting of n silica bilayers with an AB stacking sequence (denoted as n-NSs hereafter, as shown in Fig. 1). The E_R of a silica bilayer ($n = 1$) is only 0.15 eV/SiO_2, lower by nearly one order of magnitude than that of already-synthesized fibrous silica-w consisting of 2 MR units ($\sim$1.25 eV/SiO_2). It is also lower than those of the 2D silica NSs composed of 2–6 MRs whose E_R values are 0.75–0.82 eV/SiO_2