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First-principles identification of two- and four-membered-ring hybrid structures of silica nanorings

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ABSTRACT

We performed first-principles calculations to study the energetics, IR spectra, and electronic structures of silica nanorings (NR) consisting of two- and four-membered ring (2-4MR) units. A comparison study of other silica clusters, such as nanochains (NC) and nanorings formed by two-membered rings (2MRs) was made. The results show that for small-size $(SiO_2)_n$ clusters with $n < 24$, the nanochains composed of 2-4MRs (2-4MR-NCs) are more stable than other kinds of NRs and NCs. When $n > 24$ the 2-4MR-NRs structures become energetically favorable. 2-4MR-NRs have the narrowest HOMO–LUMO gaps which increase with increasing cluster size, distinctive IR spectra characterized by several peaks at the 1000–1150 cm^{-1} region.

1. Introduction

Silica nanoclusters have been the focus of much research over the past few decades, because of its potential applications in microelectronics, optical communications and catalysis. The electronic and optical properties of silica clusters differ from those of the surface of bulk materials as revealed by various experiments, ranging from light adsorption [1] to photoluminescence [2–4]. Understanding the relationship between the cluster structures and the related properties is thus highly desirable. Theoretical studies of small-size silica clusters have revealed diverse metastable building blocks with chain [5,6], ring [7–9], cage [10], and tubular [11,12] configurations formed by assembling two-, three- and four-membered rings (2MRs, 3MRs, and 4MRs). Using a global optimization algorithm, Bromley et al., predicted the ground state candidates for the $(SiO_2)_N$ cluster with $N = 6$–27 [13–15], which are more stable than the other available clusters of similar size. The structures of these clusters differ significantly from the network of silicon-centered corner-sharing SiO_4 tetrahedral of bulk silica where six-membered rings (6MRs) were found to be the most frequent. The structural features of the silica clusters are related to their high surface-to-bulk ratios that give rise to significant surface reconstruction to reduce the energy.

Among these configurations, silica nanorings (NRs) are of particular interest, because of its unique structural properties. Bromley et al. proposed a stable form of $(SiO_2)_n$ NRs resulting from the joining of the end groups of a chain made up of 2MRs to explain an experimentally found IR features [7]. Their density functional calculations showed that the NRs are energetically more stable than the corresponding linear chains for $n > 11$. Zhao et al. modeled $(SiO_2)_n$ NRs with linked 3MRs of $(SiO_2)_3$ units [8]. First-principles calculations showed that these structures are energetically more favorable at $n = 16$ and $n = 25$ than the corresponding linear chains and NRs formed on the base 2MRs. Different from the fully coordinated 2MR-NRs, these 3MR-NRs contain non-bridged-oxygen atoms (NBOs) terminating the 3MR units. Well-ordered silica nanotubes can be built via assembly of these 3MR-NRs by joining the NBOs to form additional 2MRs [12]. Silica NRs with 2MR-3MR-hybrid structures (2-3MR-NRs) have also been proposed from first-principles calculations as energetically favorable building blocks for silica nanocages and layered materials [9]. These hypothetical nanostructures enrich the database of silica nanostructures and offer opportunities for the experimental work that is seeking to realize them. However, the theoretical studies of silica NRs are

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still limited. Searching for more stable configurations of silica NRs and studying their electronic properties are both highly desirable.

In this work, we propose stable configurations of silica NRs composed of 2MR-4MR-hybrid rings (2-4MRs) and investigate their stability and electronic structures using first-principles calculations. Our calculations show that for $(SiO_2)_n$ clusters with $n < 24$, the nanochains composed of 2-4MRs (2-4MR-NCs) are more stable than other kinds of NRs and NCs, while the 2-4MR-NRs structures become energetically favorable when $n > 24$. The 2-4MR-NRs can be characterized by narrow HOMO–LUMO gaps and several peaks at the 1000–1150 cm^{-1} region in IR spectra. Although, these silica NRs and NRs are metalstable compared to the clusters reported in Ref. [14], they still have high plausibility in view of their energetic advantageous over the 2MR-based fibrous silica-*w* and NRs. The electronic structures and IR spectra predicted in this work are also available for identifying these NRs and NCs in experiments.

2. Methods and computational details

We have performed first-principles calculations using an efficient code, SIESTA [16–18], to optimized the configurations, and investigated the energetics, and electronic structures. The SIESTA is based on density functional theory adopting a localized linear combination of numerical atomic-orbital basis sets for the description of valence electrons and norm-conserving non-local pseudopotentials for the atomic core. The pseudopotentials were constructed using the Trouiller–Martins scheme [19] to describe the valence electron interaction with the atomic core; the non-local components of the pseudopotential were expressed in the fully separable form of Kleinman and Bylander [20,21]. The Perdew–Burke–Ernzerhof (PBE) form generalized gradient approximation (GGA) corrections were used for the exchange-correlation potential [22]. The atomic orbital basis set was of double-ζ quality with inclusion of polarization functions (DZP), with a split-norm value for partitioning of the zetas into inner and outer regions of 0.25. The basis functions were strictly localized within radii that corresponded to confinement energy of 0.01 Ry, with the exception of the polarization functions where a fixed radius of 6.0 Bohr was specified. An auxiliary basis set of a real-space grid was used to expand the electron density for numerical integration. A kinetic energy cutoff of 150 Ry was employed to control the fineness of this mesh.

Silica NRs and NCs were placed in a supercell with a vacuum region of up to 10 Å along the *x*, *y*, and *z* directions to ensure that isolated clusters were considered. This supercell size was converged in energy calculations within 2 meV/SiO_2 against a size with a vacuum region of 20 Å for the NRs and NCs. The equilibrium structures of silica clusters, were obtained by relaxing the atomic coordinates with a conjugate gradient (CG) algorithm, reaching a tolerance in the force of $F_{max} < 0.01$ eV/Å. The IR spectra calculations of silica NRs and NCs were preformed using *Gaussian 03* [23] at the level of B3LYP/6-31G(d). The structures of the clusters were optimized at the same level prior to IR spectra calculations.

3. Results and discussion

Two main factors, strain and the NBO ratio, affect the stabilization of silica clusters. The strain of silica clusters is mainly dominated by the size and atomic arrangement of *n*MR units. Generally, the larger the *n*MR unit ($n \leqslant 6$), the lower the strain energy involved in the clusters. NBOs are disadvantageous to the cluster stability because the silicon atoms connected to the NBOs are under-coordinated. Therefore, silica clusters which have less NBOs and lager size of the *n*MR units are more stable. In this work we focus on the NBO-free silica NRs composed of equal numbers of 2MRs and 4MRs (as shown in Fig. 1(a)). Other kinds of configurations, such as 2-4MR-NCs, 2MR-NRs, and 2MR-NCs are also presented in Fig. 1(b)–(d).

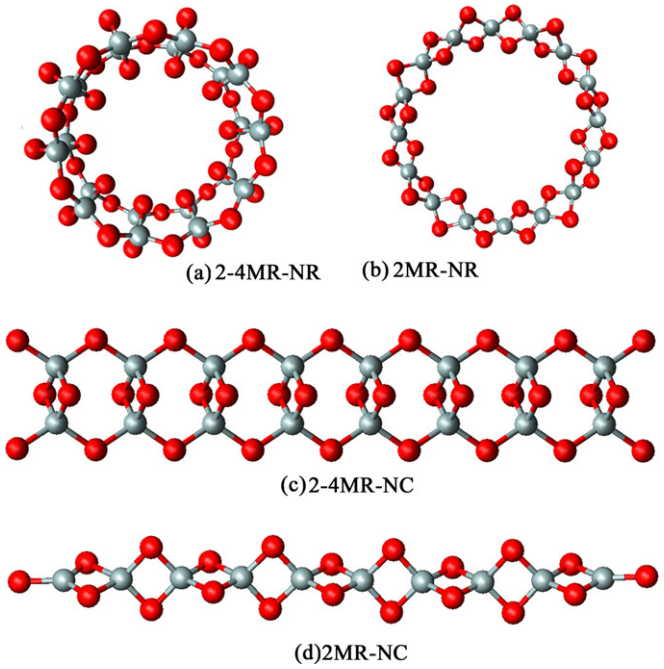

Fig. 1. The configurations of the silica NRs and NCs designed on the base of 2MR and 2-4MR units. Gray balls represent Si atoms, and red balls are O atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

The energies of these NRs and NCs relative to that of α-quartz crystal[1] are plotted in Fig. 2. It is obvious that the relative energies decrease with the increase of cluster size represented by *n*. The relative energies of 2-4MR-NRs decrease more rapidly than those of other kinds of configurations. The energy of NBO-free 2-4MR-NRs relative to α-quartz crystal mainly arises from the strain energy inherent in 2-4MR units and the curvature-related strain energy of the NRs. The later one is released rapidly with the increase of cluster size. For the 2MR-NRs, however, the energy oscillates between the lower *N*-even and the higher *N*-odd NRs, due to the mismatch strain, which is consistent with the result reported in Ref. [7]. The intersections between the variation trends of different kinds of NRs and NCs clearly show that the stable configurations are size-dependent. For the NRs and NCs with $n < 11$, the 2MR-NCs structures are most stable, followed by 2-4MR-NCs. For $11 < n < 22$, the 2-4MR-NCs are the most stable structures, whereas the NRs made up of 2-4MR hybrid units become the most favorable configurations when $n > 24$. It should be mentioned that these NRs and NCs are less stable than the ground state structures of silica clusters reported in prior literatures [13,14]. We calculated the relative energies of $(SiO_2)_{18}$ clusters with the models of Ref. [14] and 2-4MR-NC of the present work, respectively, and found that the former structure is about 0.53 eV/SiO_2 more stable than the later one.

These size-dependent stable configurations can be attributed to the compromise of the curvature-related strain energies, the strain energies inherent in nMR units, and the energy increase con-

[1] The calculations of α-quartz were performed by applying three-dimensional periodical boundary conditions along *x*-, *y*-, and *z*-directions. The Brillouin zone was sampled with a *k*-point grid of $8 \times 8 \times 8$, according to the Monkhorst–Pack scheme. All the atomic coordinates were relaxed until the maximal atomic force was below 0.01 eV/Å. The lattice vectors were also optimized simultaneously, with each component of the stress tensor below 0.02 GPa. The lattice constants obtained from the present calculations are $a = 4.88$ Å and $c = 5.41$ Å, in good agreement with the experimental data, $a = 4.92$ Å and $c = 5.40$ Å.