# A Family of Stable Silica Fullerenes with Fully Coordinated Structures

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Theoretical electronic structure techniques have become an indispensable and powerful tool for predicting molecular properties and designing new materials. The discovery of $C_{60}$ opened a challenging field in nanoscale materials science, and since then people have been looking for its inorganic analogues. On the basis of the B3LYP/6-31G(d) calculations, here we provide theoretical evidence for a family of stable silica fullerenes with fully coordinated structures, which exhibit highly structural and energetic stabilities, very large energy gaps, and extremely good resistibilities to breakdown of the insulating capability in an applied electric field. Our calculations indicate that the discrete silica fullerenes are a possible polymorph of silica and can be synthesized under some conditions. They are expected to find novel applications in silica-based molecular devices. The present results may provide an aid in the experimental design for controllably producing desired silica clusters.

## 1. Introduction

Cluster science has become quite an active research field in recent decades. The discovery of the $C_{60}$ molecule by Kroto et al.[1] in 1985 and the subsequent synthesis of carbon nanotubes (CNT) by Iijima[2] in 1991 have opened new research opportunities in science, engineering, and technology.[3−5] Since then, people have been looking for possible existence of fullerenes and nanotubes based on other elements rather than carbon.[6−13] Metal sulfides ($WS_2$ and $MoS_2$)[14,15] were first found to be able to form cages and tubes. Thereafter experimental and theoretical studies addressing this issue naturally focused on boron−nitrogen $(BN)_n$ clusters because they are isoelectronic to carbon fullerenes. Recently, typical semiconductor compounds of the group III−V family, such as AlN, GaAs, and InSb, were considered as appropriate candidates of inorganic fullerenes.[16]

Currently there is tremendous interest in studying silica clusters, including both the experimental[17−24] and theoretical[25−45] aspects, largely due to their diverse applications in microelectronics, optical communications, and thin film technology.[46−47] While effort was contributed to controllably fabricating silica nanoclusters and nanoparticles via different methods, such as laser ablation, plasma discharge, secondary ion mass spectrometry, and flame oxidation, the corresponding theoretical study attracted increasingly great attention. It is highly desired to search for novel routes for the synthesis of silica cluster-assembled materials with tailored structures and desired properties. The geometries and building principles that govern silica clusters have by now been intensively studied and well-understood. In particular, it was noted that the clusters for $n \geq 24$ ($n$ denotes the number of $SiO_2$ units) highly prefer fully coordinated structures with different caged (i.e., fullerene-like) geometries over those with terminated defects.[42,43] The discrete silica fullerenes are structurally very different from various cages in zeolites, where tetrahedron $SiO_4$ extends periodically in three-dimensional networks. Here we present a systematic study of discrete silica cages, ranging in size from $n = 12$ to 60, to understand (i) what is the general structural characteristic for silica fullerenes, (ii) whether there exist a family of discrete silica fullerenes, like carbon fullerenes, (iii) and if so, how about the structural stability and possibility to be realized for these fullerenes, and (iv) what novel electronic properties can be expected from them.

In this work, we have addressed these issues for the first time by performing density functional calculations on a series of discrete silica cages. First, we discussed the methods designing silica fullerenes, and show their structural and energetic stabilities based on the calculated results. Then, the possibility of these novel fullerenes to be realized was validated by comparing their monomer binding energies with those of the well-known carbon fullerenes. Finally, the novel electronic properties of the silica fullerenes were predicted.

## 2. Computational Method

The Gaussian 98[48] package was used and calculations were performed at the B3LYP level of theory with both the LANL2DZ and 6-31G(d) basis sets. To obtain the local minima of the desired superatomic clusters unbiasedly, full geometry optimizations without any symmetrical constraint were first undertaken at the B3LYP level with the LANL2DZ basis set. Once the point-group symmetries of the clusters were found, further optimizations were performed again using the larger 6-31G(d) basis set. To examine whether the optimized structures are stable, the harmonic vibrational frequencies were computed at the B3LYP/6-31G(d) level for the clusters with $n < 60$, and at the B3LYP/LANL2DZ level for the cluster with $n = 60$.

## 3. Results and Discussion

**3.1. Design Principle.** Bulk silica possesses tetrahedrally coordinated structures, where $SiO_4$ tetrahedrons occur in general

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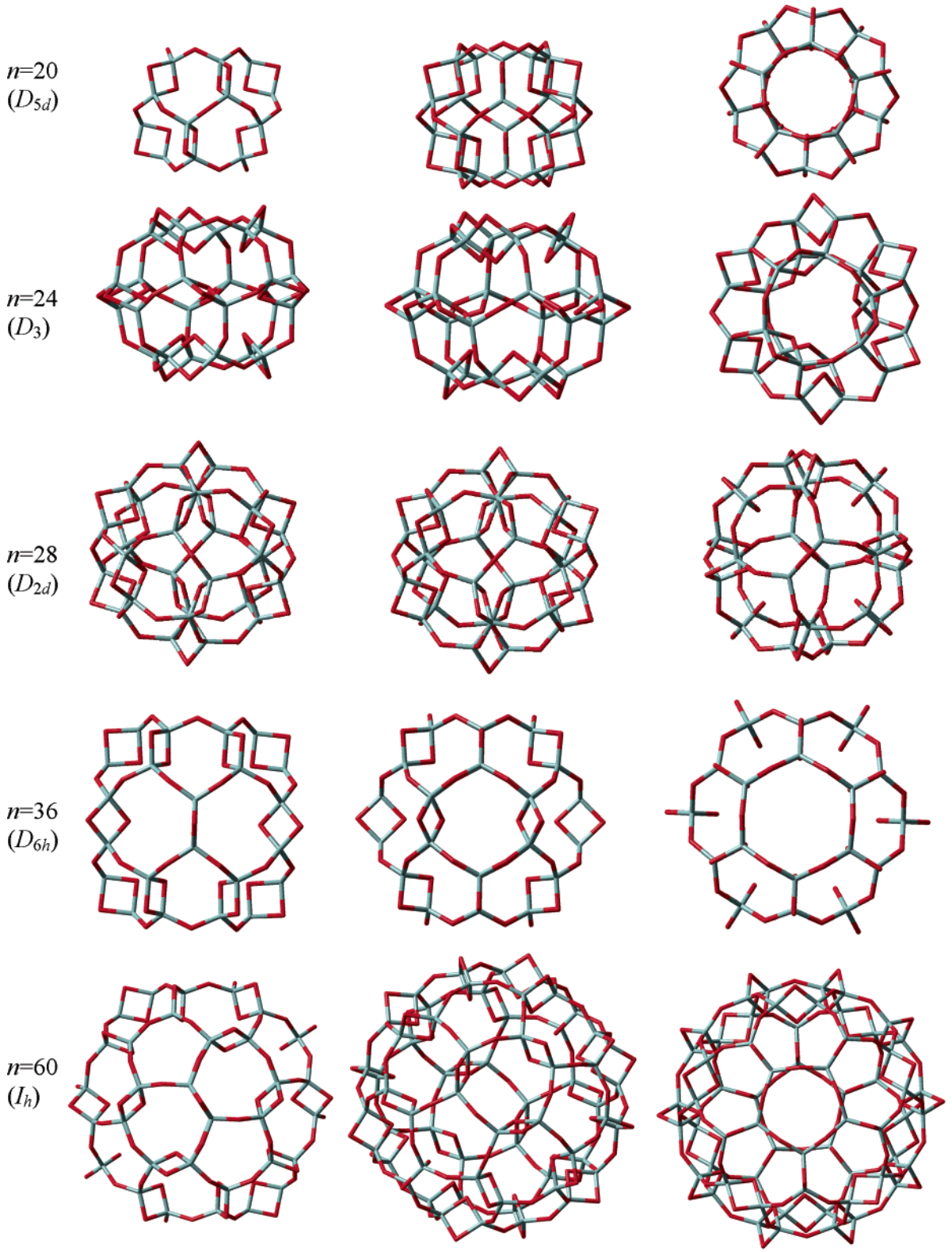


**Figure 1.** Geometries of the silica fullerenes optimized at the B3LYP/6-31G(d) level. The views along three orthogonal axes are provided to appreciate the symmetries and the shapes of the silica fullerenes.

in six- and eight-membered rings. Smaller membered rings (SMRs), such as four- (4MR), three- (3MR), and two- (2MR) membered rings, are believed to be more frequently present in nanometer-sized silica particles than in the bulk materials. By using these SMRs, several models of discrete fully coordinated silica structures, which present themselves in various cage-like and tubular forms,[42−45] have been reported. A common structural characteristic is noted in these fully coordinated clusters: $SiO_4$ tetrahedrons naturally divide into an edge-sharing set and a corner-sharing set, in other words, half of all O atoms are in double-oxygen bridges (DOBs) (or 2MRs) and the other half of O atoms are in single-oxygen bridges (SOB) (or any larger membered ring than 2MRs). Alternatively, these fully coordinated structures can be described as Si−Si frameworks averagely linked by DOBs and SOBs. In this view, discrete silica fullerenes are expected to have a family, similar to C and BN fullerenes.

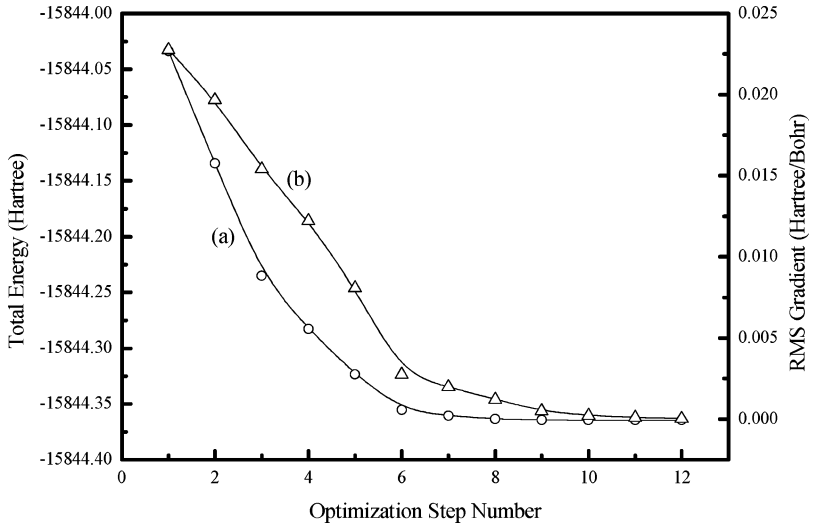


**Figure 2.** Variations of total energy for curve a and root-mean-square gradient for curve b during optimization for $(SiO_2)_{36}$ fullerene.

Several recent investigations[42,43] have dealt with, using individual design principles, the possibility of the silica cages for $n = 12$, 18 and 24. We are especially interested in the specific silica fullerenes, where Si−Si skeletons are based upon the skeletons of carbon fullerenes. A number of isomers of silica fullerenes can be constructed as Si−Si skeletons that are bridged by DOBs and SOBs. Here, we only consider the relatively symmetrical structures. Figure 1 displays some of the so-constructed silica fullerenes, $(SiO_2)_n$ ($n = 20$, 24, 36, and 60). It should be noted that the O−Si−O angles in the these silica fullerene-like structures have more or less deviations from that in the idealized $sp^3$ hybridized structures (109.5°) due to their restricted geometries. In this sense, Si atoms do not seem to be fully coordinated. However, we found that all the Si−Si distances in 2MRs are in the range of 2.37−2.40 Å, which are only slightly larger than those in the bulk (2.25 Å). This fact indicates that the Si atoms in 2MRs have formed the covalent bonds with each other to some extent to make themselves in fully coordinated surroundings. Thus the cage-like structures presented in the present work can be considered as fully coordinated structures.

**3.2. Geometries.** Under the design principle, we have considered the $D_{5d}$ isomer for the cluster with $n = 20$, $D_3$ and $C_{6v}$ isomers for the cluster with $n = 24$, the $D_{2d}$ isomer for the cluster with $n = 28$, the $D_{6h}$ isomer for the cluster with $n = 36$, and the $I_h$ isomer for the cluster with $n = 60$. The optimized geometries are shown in Figure 1.

A first test of the viability of the proposed fullerenes is given by inspecting the variations of their total energies and root-mean-square gradients during optimization. As an example, Figure 2 shows calculated results at the B3LYP/6-31G(d) level for the $(SiO_2)_{36}$ fullerene. We found that the originally designed structures rapidly and monotonically converge for both the total energy (curve a) and the root-mean-square gradient (curve b) to its local minimum on the potential energy surface (PES) with only 12 steps of optimization. The same holds true for other silica fullerenes considered. Under geometry optimizations all clusters exhibit high point group symmetries as well as nearly uniform shapes, as shown in Figure 1. The frequency calculations for the optimized structures show all the frequencies are real, suggesting these silica fullerenes are really local minima on the PESs. These observations indicate that the proposed silica fullerenes are structurally rigid and energetically stable enough in nature.

**TABLE 1: Calculated Binding Energies ($E_b$), HOMO and LUMO Energies, and HOMO-LUMO Gaps ($E_g$) of Investigated Silica Fullerenes**

| $n$ | symmetry | $E_b$ (eV) | $E_{HOMO}$ (hartree) | $E_{LUMO}$ (hartree) | $E_g$ (eV) |
|---|---|---|---|---|---|
| 20 | $D_{5d}$ | −4.997 | −0.32600 | −0.08923 | 6.443 |
| 24 | $D_3$ | −5.141 | −0.33361 | −0.08576 | 7.003 |
| 28 | $C_{6v}$ | −5.208 | −0.34155 | −0.07838 | 7.161 |
| 36 | $D_{6h}$ | −5.255 | −0.33951 | −0.07763 | 7.126 |
| 60 | $I_h$ | −5.313 | −0.35244 | −0.07473 | 7.557 |
| α-quartz | | −6.075 | | | 9.2[a] |

[a] References 55−57.

**3.3. Binding Energies.** Apart form geometrical aspects, the stabilities of these silica fullerenes can be tested by computing the monomer binding energy ($E_b$), defined as $E_b = [nE(SiO_2) - E(SiO_2)_n]/n$, where $E(SiO_2)$ is the energy of a isolated $SiO_2$ monomer and $E(SiO_2)_n$ is the total energy of the cluster $(SiO_2)_n$. To establish a comparable criterion, we calculated the $E_b$ of α-quartz, the most stable phase for bulk silica, using Siesta 1.3 code.[49] The calculation was performed with use of a supercell containing 24 $SiO_2$ units with periodical boundary conditions along three directions. The binding energy is found to be 6.075 eV at the Perdew−Burke−Ernzerhof's Generalized Gradient Approximation (GGA) functional[50] with the double-ζ plus polarization orbital (DZP). The $E_b$'s values for the silica fullerenes at the B3LYP/6-31G(d) level were summarized in Table 1. It is noted that these values are not far from the limiting value of α-quartz, and are comparable to the corresponding atomization enthalpy per atom of gas-phase $C_{60}$, a value of about 7 eV,[51] indicating the thermodynamic accessibility of the proposed molecular cages. In Figure 3, we plot the calculated $E_b$ as a function of the inverse number of $SiO_2$ units $1/n$, a scale factor of the curvature of the cage. There is a dependence of $E_b$ on the cluster size, which was well fitted by a linear slope with a limiting value for $1/n \rightarrow 0$. This $1/n$ linear behavior has also been found for carbon[52,53] and BN[54] fullerenes and attributed to strain due to the deviation of the cage surface from planarity. In the case of the present silica fullerenes the $1/n$ dependence of $E_b$ is due to the combined strain effects of the curvature of cages and the 2MRs contained in cages.

**3.4. Energy Gaps.** Since bulk silica is a good insulator material with a large gap, such as around 9 eV for α-quartz,[55−57] it is interesting to study how this energy gap evolves with reduced size. In Table 1 we listed the calculated HOMO and LUMO energies, and the corresponding HOMO-LUMO gaps

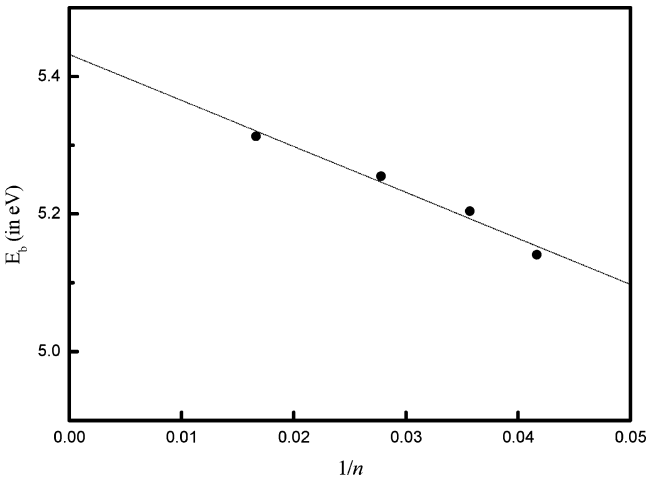


**Figure 3.** Binding energy ($E_b$) of the silica fullerenes as a function of the inverse number of $SiO_2$ units $1/n$. The dotted line is the linear fit of the data.

of the different size silica fullerenes. Clearly, the energy gaps are large enough, which are a signature of their highly chemical stabilities once they are formed. This fact suggests the isolated $SiO_2$ fullerenes retain good insulating capability of their bulk and may make novel applications in $SiO_2$-based nanotechnology. With reducing size, the varieties of HOMO and LUMO show different trends: the HOMO, which mainly consists of the lone-pair orbitals on O atoms, rises due to quantum confinement over the range, whereas the LUMO, which is characterized by large contributions from partly occupied p orbitals on Si atoms with some admixture of O-based orbitals, descends. Thus the HOMO-LUMO gap shows a decreasing trend.

**3.5. Behavior in an Applied Electric Field.** According to the present calculations, the silica fullerenes can be very good insulating materials, as indicated by their large values of HOMO-LUMO gaps. In many practical applications, insulating materials will be in an applied electronic field. So apart from size, an applied field can be used as another important parameter to modulate the structure and property of nanoscale devices. The insulating materials, however, will be broken down (i.e., the HOMO/LUMO energy levels will cross and the gap will close) as the applied electronic field is large enough. In this sense, it is interesting to study the transitions of structure and property induced by an external electric field from the point of view of practical applications, which is of crucial importance in fabricating novel nanodevices.

We have chosen the smallest silica fullerene $(SiO_2)_{20}$ as a representative considering its relatively smaller size and hence feasible CPU cost. Applying a uniform finite electric field along the direction of the quintic axis, we performed fully geometrical optimization for the silica fullerene at the B3LYP/6-31G(d) level. The magnitude of applied field varies from 25.7 to 257 MV $cm^{-1}$. We found this silica fullerene almost retains its graceful geometry, i.e., does not collapse and rupture, throughout the whole simulation, even in the field as strong as 257 MV $cm^{-1}$, indicating its intrinsically structural rigidity and stability. Further, we inspected its HOMO, LUMO, and HOMO-LUMO gap variation with the increasing field intensity. As Figure 4 shows, both the HOMO and LUMO levels almost linearly vary with the increasing field intensity but in opposed directions: the former monotonically increases, in contrast with the HOMO level decrease of the silica nanowire calculated by Sun et al.,[58] whereas the latter decreases over the range, and hence the HOMO-LUMO gap decreases and a cross between the HOMO and LUMO levels would occur at some applied electric field.

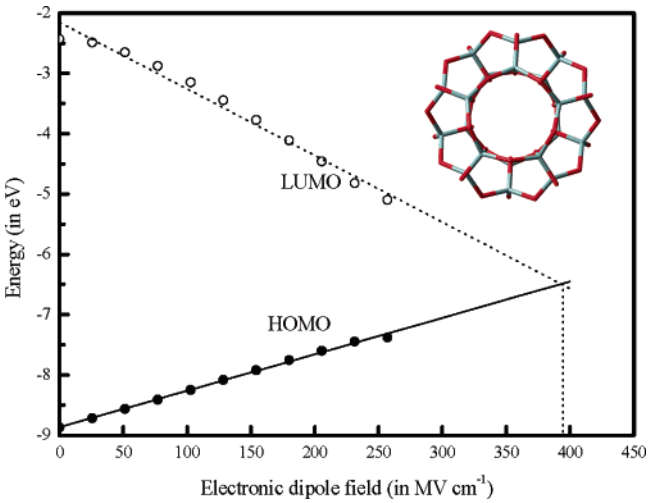


**Figure 4.** Variation of the HOMO and LUMO energies of the $(SiO_2)_{20}$ fullerene with applied electric dipole field. Filled dots and the solid line indicate the calculated and fitted HOMO levels, and the empty dots and the dotted line are calculated and fitted LUMO levels, respectively.

The magnitude of the field corresponding to the intersection is referred to as the "breakdown threshold", which corresponds to the breakdown of an insulation material by an applied electric field, and is a very important quantity for understanding the insulating property of materials. The breakdown behavior can be correlated with the polarizing effect of the electronic field on wave functions and energies. Static electronic field induces a dipole, which causes a shift of electron density from the induced positive end of the molecule to the induced negative end, and hence results in the redistribution of the energy levels and compositions of molecular orbitals. As a result of the polarizing effect of the electronic field, the electron-donating HOMO and electron-accepting LUMO are destabilized and stabilized, respectively, due to the increase of the Coulomb repulsion and Coulomb attraction near the frontier MOs, respectively, hence the HOMO/LUMO gap is reduced and finally is closed by a large enough field. To estimate the breakdown threshold, we fitted and extrapolated the calculated data. As seen from Figure 4, both the dependences of the HOMO and LUMO on electric field were well fitted linearly, and the breakdown threshold is around 396 MV $cm^{-1}$. This value is much larger than the value for the breakdown fields of high quality $SiO_2$ (13.5 MV $cm^{-1}$),[59,60] also than that for the $SiO_2$ film, 18−27 MV $cm^{-1}$,[61] and even than the previously calculated result for the edge-sharing $SiO_2$ nanowire, 22 MV $cm^{-1}$.[58] This fact indicates that the nanosized silica cages are highly resistive to external electric fields, and can be used as a good insulating coat. In particular, it is noted that the graceful geometry of the cage still remained even as it is broken, indicating the reversibility of the breakdown. Further, it is interesting to know how sensitive the gap and hence the breakdown threshold is to the cage size and the electronic field direction. We have performed calculations for the silica fullerene with $n = 24$ in applied electronic fields, and also for the silica fullerene with $n = 20$ as the directions of applied fields (50 MV $cm^{-1}$) are along $x$, $y$, and $z$ axes, respectively. The calculated results show that the breakdown threshold of the cage for $n = 24$ was found to be 35 MV $cm^{-1}$ larger than that of the cage for $n = 20$, and that the gaps of the fullerene with $n = 20$ are 6.190, 6.193, and 6.231 eV, as the directions of applied fields (50 MV $cm^{-1}$) are along $x$, $y$, and $z$ axes, respectively. These results clearly indicate

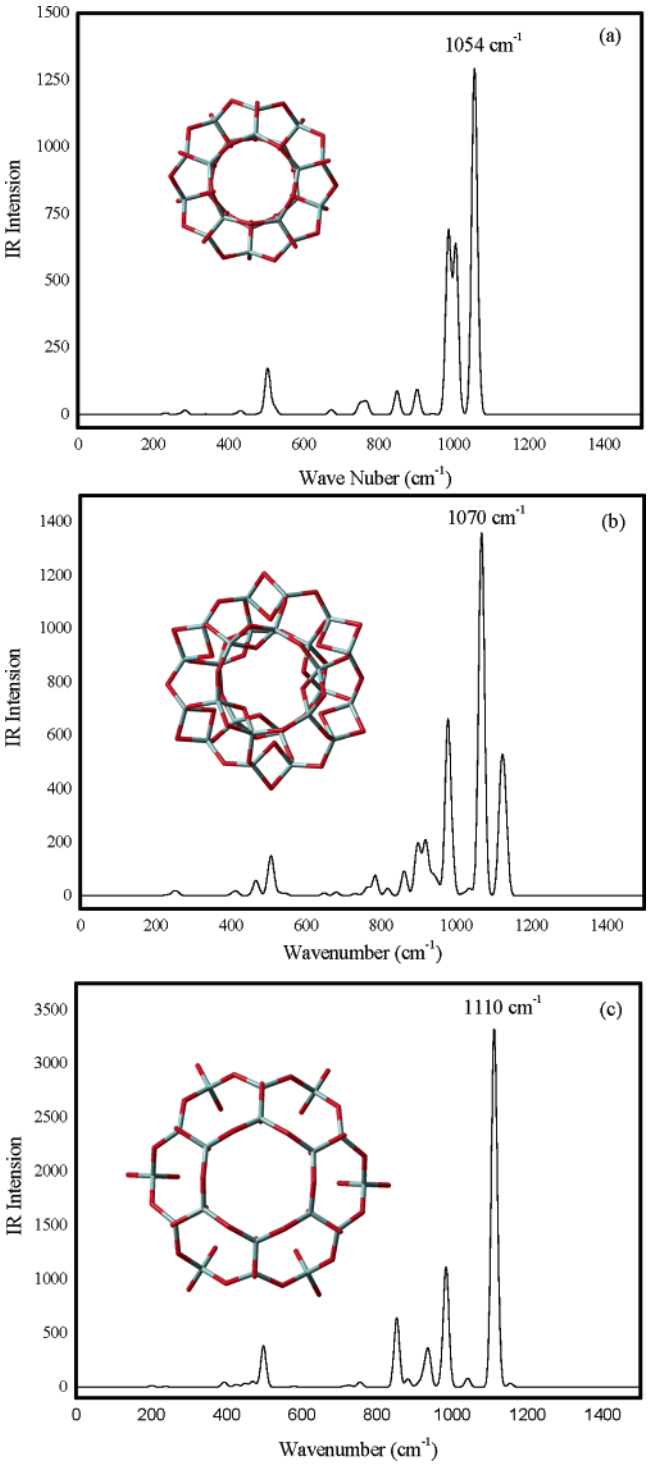


**Figure 5.** Calculated vibrational spectra for three silica fullerenes: (a) $n = 20$, (b) $n = 24$, and (c) $n = 36$.

that the breakdown threshold increases with the cage size, but is not sensitive to the directions of applied electronic fields.

**3.6. IR Spectra.** As illustrated by Figure 5 the frequency calculations show that there are a few extraordinarily prominent modes in the IR spectra. The highest infrared active mode is at 1054 $cm^{-1}$ for $n = 20$, 1070 $cm^{-1}$ for $n = 24$, and 1100 $cm^{-1}$ for $n = 36$, respectively. Clearly, these strongest modes show a red shift trend with increasing size, which is consistent with the fact that the ring stain decreases with increasing cluster size. These modes can be assigned mainly to the asymmetrical stretching vibrationals of the bridging Si−O bonds, while those below 1000 $cm^{-1}$ were attributed to the Si−O bond vibrations in 2MRs. These characteristic spectral signatures should provide good opportunities for the experimental detection of these silica fullerenes by infrared matrix isolation spectroscopy.

## 4. Conclusions

In summary, we have considered a few well-defined stoichiometric family of silica fullerenes ranging in size from 20 to 60 $SiO_2$ units. Our DFT calculations show that the desired structures have highly energetic stabilities, large HOMO-LUMO gaps, and good resistibilities to rupture of insulating capability in external electric fields. These silica fullerenes are a possible polymorph of silica and can be expected to find potential applications in many fields, such as catalysis, controlled delivery, artificial cells, and light fillers, mainly making use of their characteristic geometrical structures (nanosized pores) and novel electronic properties (large gap and good insulating capability). We hope that this work will stimulate experimental groups to widen their searches for heterofullerenes and tailored silica nanodevices.

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## References and Notes

(1) Kroto, H. W.; Health, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
(2) Iijima, S. *Nature* **1991**, *354*, 56.
(3) Kuzmany, H.; Fink, J.; Mehring, M.; Roth, S. *Fullerenes and Fullerene Nanostructures*; World Scientific: Singapore, 1996.
(4) Cioslowski, J. *Electronic Structure Calculations on Fullerenes and Their Derivatives*; Oxford University Press: New York, 1995.
(5) Hirsch, A. *Fullerenes and Related Structures*; Springer: Berlin, Germany, 1999; Vol. 199, p 246.
(6) Taylor, P. R.; Bylaska, E.; Weare, J. H.; Kawai, R. *Chem. Phys. Lett.* **1995**, *235*, 558.
(7) Raghavachari, K.; Zhang, B.; Pople J. A.; Johnson B. G.; Gill, P. M. W. *Chem. Phys. Lett.* **1994**, *220*, 385.
(8) Strout, D. L. *J. Phys. Chem. A* **2000**, *104*, 3364.
(9) Alexandre, S. S.; Mazzoni, M. S. C.; Chacham, H. *Appl. Phys. Lett.* **1999**, *75*, 61.
(10) Chopra, N. G.; Luyren, R. J.; Cherry, K.; Crespi, V. H.; Cohen, M. L.; Louis, S. G.; Zettl, A. *Science* **1995**, *269*, 966.
(11) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444.
(12) Feldman, Y.; Wasserman, E.; Srolovita, D. J.; Tenne, R. *Science* **1995**, *267*, 222.
(13) Pattanayak, J.; Kar, T.; Scheiner, S. *J. Phys. Chem. A* **2002**, *106*, 2970.
(14) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444.
(15) Margulis, L.; Salitra, G.; Tenne, R.; Talianker, M. *Nature* **1993**, *365*, 113.
(16) Chang, Ch.; Patzer, A. B. C.; Sedlmayr, E.; Steinke, T.; Sulzel, D. *Chem. Phys. Lett.* **2001**, *350*, 399.
(17) Iraqi, M.; Goldberg, N.; Schwarz, H. *J. Phys. Chem.* **1993**, *97*, 11371.
(18) Goldberg, N.; Iraqi, M.; Koch W.; Schaltz, H. *Chem. Phys. Lett.* **1994**, *225*, 404.
(19) Fan, J.; Nicholas, J. B.; Price, J. M.; Colson, S. D.; Wang, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 5417.
(20) Lafargue, P. E.; Gaumet, J. J.; Muller, J. F. *J. Mass Spectrom.* **1996**, *31*, 623.
(21) Wang, L. S.; Nicholas, J. B.; Dupuis, M.; Wu, H.; Colson, S. D. *Phys. Rev. Lett.* **1997**, *78*, 4450.
(22) Glinka, Y. D.; Lin, S. H.; Lin, Y. T.; Chen, Y. T. *Phys. Rev. B* **2000**, *62*, 4733.
(23) Altman, I. S.; Lee, D.; Chung, J. D.; Song, J.; Choi, M. *Phys. Rev. B* **2001**, *63*, 161402.
(24) Uchino, T.; Aboshi, A.; Kohara, S.; Ohishi, Y.; Sakashita, M.; Aoki, K. *Phys. Rev. B* **2004**, *69*, 155409.
(25) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1993**, *97*, 5875.

(26) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1995**, *103*, 1057.
(27) Harkless, J. A. W.; Stillinger, D. K.; Stillinger, F. H. *J. Phys. Chem.* **1996**, *100*, 1098.
(28) Nayak, S. K.; Rao, B. K.; Khanna, S. N.; Jena, P. *J. Chem. Phys.* **1998**, *109*, 1245.
(29) Chelikowsky, J. R. *Phys. Rev. B* **1998**, *57*, 3333.
(30) Xu, C.; Wang, W.; Zhang, W.; Zhuang, J.; Liu, L.; Kong, Q.; Zhao, L.; Long, Y.; Fan, K.; Qian, S.; Li, Y. *J. Phys. Chem. A* **2000**, *104*, 9518.
(31) Nedelec, J. M.; Hench, L. L. *J. Non-Cryst. Solids* **2000**, *277*, 106.
(32) Chu, T. S.; Zhang, R. Q.; Cheung, H. F. *J. Phys. Chem. B* **2001**, *105*, 1705.
(33) Zhang R. Q.; Chu, T. S.; Cheung, H. F.; Wang, N.; Lee, S. T. *Phys. Rev. B* **2001**, *64*, 113304.
(34) Song, J.; Choi, M. *Phys. Rev. B* **2002**, *65*, 241302.
(35) Flikkema, E.; Bromley, S. T. *Chem. Phys. Lett.* **2003**, *378*, 622.
(36) Flikkema, E.; Bromley, S. T. *J. Phys. Chem. B* **2004**, *108*, 9638.
(37) Umari, P.; Gonze, X.; Pasquarello, A. *Phys. Rev. Lett.* **2003**, *90*, 027401.
(38) Lu, W. C.; Wang, C. Z.; Ho, K. M. *Chem. Phys. Lett.* **2003**, *378*, 225.
(39) Lu, W. C.; Wang, C. Z.; Nguyen, V.; Schmidt, M. W.; Gordon, M. S.; Ho, K. M. *J. Phys. Chem. A* **2003**, *107*, 6936.
(40) Zhang, D. J.; Zhang, R. Q. *Chem. Phys. Lett.* **2004**, *394*, 437.
(41) Bromley, S. T.; Zwijnenburg, M. A.; Maschmeyer, Th. *Phys. Rev. Lett.* **2003**, *90*, 035502.
(42) Bromley, S. T. *Nano Lett.* **2004**, *4*, 1427.
(43) Zhang, D. J.; Zhao, M. W.; Zhang, R. Q. *J. Phys. Chem. B* **2004**, *108*, 18451.
(44) Zhang, D. J.; Zhang, R. Q. *J. Phys. Chem. B* **2006**, 110, 1338.
(45) Zhang, D. J.; Zhang R. Q.; Han, Z.; Liu C. B. *J. Phys. Chem. B* **2006**, *110*, 8992.
(46) Helms, C. R.; Deal, B. E., Eds. *The Physics and Chemistry of $SiO_2$ and the $Si-SiO_2$ interface*; Plenum Press: New York, 1988.
(47) Suzuki, K.; Ikari, K.; Imai, H. *J. Am. Chem. Soc.* **2004**, *126*, 462.
(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(49) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Mater.* **2002**, *14*, 2745.
(50) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(51) Steele, W. V.; Chirico, R. D.; Smith, N. K.; Billups, W. E.; Elmore, P. R.; Wheeler, A. E. *J. Phys. Chem.* **1992**, *96*, 4731.
(52) Cioslowski, J. *Chem. Phys. Lett.* **1993**, *216*, 389.
(53) Seifert, G.; Vietze, K.; Schmidt, R. *J. Phys. B* **1996**, *29*, 1468.
(54) Seifert, G.; Fowler, P. W.; Mitchell, D.; Mitchell, D.; Porezag, D.; Frauenheim, Th. *Chem. Phys. Lett.* **1997**, *268*, 352.
(55) Xu, Y.; Ching, W. Y. *Phys. Rev. B* **1991**, *44*, 11048.
(56) Fisher, B.; Pollak, R.; Distefano, T.; Grobman, W. *Phys. Rev. B* **1997**, *15*, 3193.
(57) Klein, G.; Chun, H. *Phys. Status Solid B* **1972**, *49*, 167.
(58) Sun, Q.; Wang, Q.; Kawazoe, Y.; Jena, P. *Nanotechnology* **2004**, *15*, 260.
(59) Murrell, M. P.; Welland, M. E.; O'Shea, S. J.; Wong, T. M. H.; Barnes, J. R.; McKinnon, A. W.; Heyns, M.; Verhaverbeke, S. *Appl. Phys. Lett.* **1993**, *62*, 786.
(60) Sofield, C. J.; Stoneham, A. M. *Semicond. Sci. Technol.* **1995**, *10*, 215.
(61) Pompl, T.; Engel, C.; Wurzer, H.; Kerber, M. *Microelectron. Reliab.* **2001**, *41*, 543.