Ultrastable Silicon Nanocrystals due to Electron Delocalization

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Supporting Information

ABSTRACT: We report a new nanocrystalline form of silicon that gives birth to pure hydrogenated silicon nanocrystals that absorb light in the ultraviolet, visible, and infrared spectral region despite their small size of only 1 nm and without the need for expensive or toxic metal atoms. On the basis of first-principles calculations, we demonstrate that those pure, overcoordinated silicon nanocrystals are more stable than any other known silicon nanocrystals due to electron delocalization and that they form spontaneously via self-assembly. Therefore, we predict their immediate application in fields ranging from photovoltaic and light-emitting devices to photothermal cancer treatment.

KEYWORDS: Electron-deficiency, silicon nanocrystals, silicon aromaticity, photothermal cancer treatment, light emitting diodes, photovoltaics

Silicon nanocrystals (SiNC) have been attracting interest in many fields of nanoscience and nanotechnology for a long time, not only because of the high abundance and nontoxicity of silicon, but also because of their quantum confinement that makes it possible to tune their absorption and emission spectra by simply changing their size.\(^1\)\textsuperscript{\textendash}\textsuperscript{6} So far, however, the spectral absorption tuning of pure SiNC is limited to the ultraviolet frequency range.\(^7\) To extend the response to the visible and infrared region, metal atoms are often incorporated in the nanocrystals.\(^8\textsuperscript{\textendash}20\) Unluckily, those metals are often expensive or toxic. Taking advantage of the sometimes surprising nature of chemical bonds in nanoscale objects, we present here a fundamentally novel approach that is based on structure-induced electron-deficiency to cause strong electron delocalization. On the basis of first-principles calculations, we demonstrate that the resulting pure silicon nanocrystals are unusually stable and do not only absorb light in the ultraviolet, but also in the visible and infrared spectral region without the need for any metal atoms.

In contrast to carbon, silicon is less electronegative than hydrogen and it does in general not get involved in configurations where it has less than four neighbors and rather favors overcoordination.\(^21\)\textsuperscript{\textendash}25\) Such an overcoordination, however, leads to bonds that are poor in electrons. In aromatic carbon compounds, there are in general too many electrons to be accommodated in only single bonds between all involved carbon atoms. On the contrary, for the silicon atoms of the electron-deficient nanocrystals presented here there are not quite enough electrons for single bonds between all involved silicon atoms. In both cases, however, nature resolves this problem of having either too many or not quite enough electrons by delocalizing the participating electrons and we shall see how extremely stable silicon nanocrystals with aromatic-like properties result.

Overcoordinated hydrogenated silicon nanocrystals have previously been observed\(^26\) and shown to form spontaneously via self-assembly\(^27\) in pulsed SiH\(_4\)/H\(_2\) plasmas operated close to dusty plasma conditions. Among those reported nanocrystals; we will focus here on one precise example that combines overcoordination with highly symmetrical ring structures. To this end, we compare the reported Si\(_{19}\)H\(_{12}\) nanocrystal to the stable Si\(_{18}\)H\(_{24}\) finite nanotube, which is the hexagonal analogue to the pentagonal Si\(_{19}\)H\(_{12}\) discussed in detail in ref 28. This Si\(_{18}\)H\(_{24}\) nanocrystal can be characterized by three parallel and perfectly planar hexagons (see Figure 1a). Using the Gaussian software package (see Supporting Information for details), we have optimized this empty structure at different levels of theory and we have assured that it is potentially stable (i.e., it does not exhibit any imaginary frequencies at any level of theory). The resulting optimized Si\(_{18}\)H\(_{24}\) structure has B3LYP and MP2 energies of \(-5218.49\) and \(-5211.64\) hartree, respectively, which gives it about the same binding energy per atom as its pentagonal analogue of ref 28. All silicon atoms are four-times coordinated in this finite nanotube.

Upon introduction of one additional silicon atom close to the center of this Si\(_{18}\)H\(_{24}\) nanostructure, we obtain the optimized Si\(_{19}\)H\(_{12}\) structure that actually gains \((5.1 \pm 0.3)\) eV in stability that clearly exceeds not only the cohesive energy of comparable clusters of about \(-3.8\) eV\(^{29,30}\) but even the one of bulk silicon of \(-4.6\) eV\(^{31,32}\) that is, the binding is too strong to be understood in the framework of regular covalent silicon bonds. Using known cohesive energies for silicon and hydrogen,\(^{29,30}\) we find actually that the proposed Si\(_{19}\)H\(_{12}\) structure exceeds the experimentally known Si\(_{19}\)H\(_{24}\) clusters\(^{33}\) by more than 6 eV in stability. A frequency analysis confirms the vacuum stability of the Si\(_{19}\)H\(_{12}\) nanostructure since there are no imaginary frequencies and the lowest frequencies are around 90 cm\(^{-1}\). Furthermore, we have used molecular dynamics techniques to heat the structure to 1200 K.

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Even at these extreme conditions and despite the resulting large vibrational amplitudes, the Si$_{19}$H$_{12}$ structure remains thermally stable. A natural bond orbital (NBO) analysis$^{34}$ reveals that most silicon—silicon bonds in Si$_{18}$H$_{12}$ are, indeed, electron-deficient.$^{35}$ For example, the $\sigma_{\text{Si-Si}}$ bonds are severely depleted both for the six bonds of the central silicon hexagon (1.6440 electrons) and for all bonds between next neighbor silicon atoms belonging respectively to an external and the central hexagon (1.8445 electrons). The NBO analysis further unveils that the unexpected stability can be traced back to the highly delocalized nature of the electrons shared between the center silicon atom and its neighbors. When actually adding up all electrons that are “missing” in the bonds of the electron-deficient Si$_{18}$H$_{12}$ structure, we find precisely six electrons that are thus available for delocalization. While this number does obey the $(4n + 2)$ Hückel’s rule for aromaticity, this coincidence has to be considered fortuitous since Si$_{18}$H$_{12}$ is neither monocyclic nor two-dimensional.

As a consequence of this electron delocalization, we show in Figure 2 that the magnetic shielding for the Si$_{19}$H$_{12}$ nanostructure exhibits an aromatic-like behavior over its entire longitudinal axis that is more than three times stronger than that of benzene C$_6$H$_6$. To estimate to which amount the demonstrated magnetic shielding might be due to possible effects from the $\sigma$-framework,$^{36}$ we display also in Figure 2 the shielding values determined in the same way as above for the empty Si$_{18}$H$_{12}$ nanotube. Since this structure appears to be non aromatic, we can conclude that the magnetic shielding determined here for the filled Si$_{19}$H$_{12}$ nanotube can primarily be traced back to p-electrons that are delocalized between the center silicon atom and its neighbors.

To acquire a less local characteristic, we have also evaluated the global magnetic susceptibility exaltation, $\Lambda$, of the proposed Si$_{19}$H$_{12}$ nanocrystal.$^{36}$ To this end, we have used the IGAIM method$^{37}$ to calculate the magnetic properties of both the empty and the filled finite nanotubes. As a result, we find magnetic susceptibilities of $-155$ and $-255$ cgs-ppm for Si$_{18}$H$_{12}$ and Si$_{19}$H$_{12}$, respectively, leading to an approximated exaltation of $-100$ cgs-ppm.
This value is considerably larger than that of benzene ($-13.4$ cgs-ppm) further supporting our claim that the filled silicon nanostructure shows a marked aromatic-like behavior in spite of the underlying overcoordination or electron-deficiency concept.

Because of the presence of the stabilizing center silicon atom, the electronic and optical properties are also drastically different for the empty and the filled finite nanotubes. The highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) gap, for instance, calculated at the MP2 (Møller–Plesset second order perturbation theory) level for the MP2 optimized geometries decreases from 7.05 eV for the empty Si$_{18}$H$_{12}$ nanotube to 4.25 eV for the filled Si$_{19}$H$_{12}$ nanocrystal. In Figure 3, we display the corresponding density of states analyses.

The additional peak that appears in the forbidden gap of the empty Si$_{18}$H$_{12}$ nanotube due to the insertion of the center Si atom corresponds to the HOMO of the Si$_{19}$H$_{12}$ nanocrystal which we present in Figure 4. In Supporting Information, we illustrate the severe difference between the frontier molecular orbitals of the filled and the empty finite nanotubes (compare Figures S1 and S2, respectively).

In the same way, we show in Figure 5 how the optical absorption spectrum that is limited to the ultraviolet for the empty structure extends through the visible until the infrared region due to the insertion of the center silicon atom. Needless to say that such an extension of spectral response might readily lead to the environmentally friendly replacement of other expensive or toxic nanocrystals by the presently proposed ones. This replacement might lead to immediate applications in the most various fields of research reaching from potential cancer treatment where the use of gold and silver nanoparticles has been proposed since the resulting laser light absorption at about 800 nm (see Figure 5) yields optimal efficiency to photovoltaic devices where PbS, PbSe, CdS, and CdSe based quantum dots are presently employed to extend energy conversion from the ultraviolet to the infrared region. The proposed overcoordinated SiNC might also be considered for being added to the conventional SiNC employed in recent solar cell and light-emitting diode devices that ingeniously combine the properties of semiconductor nanocrystals with conjugated polymers.

Figure 4. Different views of the isovalue contour plots of the HOMO representing the electron density obtained at the B3LYP/6-311++G** level with an isovalue of 0.02 e/Å$^3$ for the filled Si$_{19}$H$_{12}$ nanocrystal: (a) side, (b) vertical cut through side, (c) top, and (d) bottom view. Note the involvement of the center silicon atom for the electron distribution of the HOMO. A catalogue of many other typical molecular orbitals can be found in the online Supporting Information section; there, one may also compare the frontier molecular orbitals of the filled and the empty finite nanotubes.

Figure 5. Absorption spectra of Si$_{18}$H$_{12}$ and Si$_{19}$H$_{12}$; that is, a comparison between an empty and a filled finite hydrogenated silicon nanotube. Because of the presence of the inner silicon atom, the latter nanocrystal does not only absorb light in the ultraviolet region, but also in the visible and in the infrared.
Since the authors obtained the best results with the smallest investigated nanocrystals and since the SiNC proposed here absorb light in a much broader spectral range than their conventional ones, the recently reported excellent device performance might yet be improved by the addition of our overcoordinated SiNC in their nanocrystal layer.

In summary, we propose for the first time the concept of electron delocalization in electron-deficient hydrogenated silicon nanocrystals leading to aromatic-like behavior. This novel phenomenon seems to be inherently connected to the unique intermediate position that nanoscale objects take between structures of molecular and microscopic dimensions. Because of the absence of formal multiple bonds, we define “electron-deficiency aromaticity” as a chemical property in which the addition of one atom to a saturated silicon ring structure causes an increase of stability that exceeds the corresponding cohesive energy as a result of the induced electron delocalization. We have demonstrated that the additional silicon atom placed in the center of an otherwise four-times coordinated parent nanostructure is not merely a weakly attached innocent bystander, but it transforms essentially and strongly the bonding relationships between all atoms of the concerned nanocrystal. The proposed nanocrystals are predicted to remain thermally stable at temperatures exceeding 1000 K. This high stability makes their experimental synthesis very likely and facilitates their applications. In addition, their properties perfectly comply with those expected for aromatic substances: first, all three hexagons are perfectly planar; second, all silicon—silicon bonds within each of the three hexagons are equivalent in length; third, the introduction of the center silicon atom increases the stability by more than the cohesive energy of bulk silicon which cannot be understood on the basis of regular covalent silicon bonds and which makes them more stable than the experimentally known Si_{29}H_{24} nanocrystal; fourth, there are six electrons being delocalized; and finally, both its magnetic susceptibility exaltation and its magnetic shielding exceed the ones of benzene.

In conclusion, based on first-principles calculations we demonstrate that pure hydrogenated silicon nanocrystals with overcoordinated ring structures can absorb light not only in the ultraviolet, but also in the visible and infrared spectral region despite their small size of about 1 nm and without the need for expensive or toxic metal atoms. Because of the addition of one single Si atom to an otherwise four-times coordinated structure, those nanocrystals manifest extremely strong electron delocalization that makes them more stable than any other known silicon nanocrystals. The strongly delocalized nature of their electronic structure gives them outstanding mechanical, chemical, electronic, and optical properties. Not only do those nanocrystals form spontaneously under appropriate experimental conditions, but their nontoxicity, low-cost, and compatibility with existing silicon-based chip-fabrication lines promise those overcoordinated Si nanocrystals an attractive future in various emerging nanotechnological domains. Of course, the present concept is not limited to the structure discussed here, but can immediately be applied to a vast number of other silicon nanoentities, including infinite systems in one or two dimensions.

ASSOCIATED CONTENT

5 Supporting Information. All calculational details and supplementary figures depicting a catalogue of important molecular orbitals are included in the Supporting Information. This material is available free of charge via the Internet at: http://pubs.acs.org.

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REFERENCES