Colloidal Synthesis of an Exotic Phase of Silicon: The BC8 Structure

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S *Supporting Information*

ABSTRACT: Creating allotropes and polymorphs of nanoparticles (NPs) has gained tremendous momentum in recent times. Group 14 (C, Si, Ge) has a number of allotropes; some with significant applications. Here we report the synthesis of Si NPs crystallizing in the BC8 structure via a colloidal route for the first time. The BC8 structure is a metastable structure of Si that can be accessed from the β-Sn form through the release of high pressure. These Si BC8 structured NPs were synthesized via reduction of SiI_4 with *n*-butyllithium, capped with octanol and precipitated from solution. The transmission electron microscopy lattice fringes as well as the selected area electron diffraction pattern of the precipitate are consistent with the BC8 structure. The LeBail whole profile fitting of powder X-ray diffraction data also confirms the structure as the BC8 phase. The Raman spectrum provides further evidence to support the BC8 structure. With proper tuning of the band gap these NPs could be potential candidates for solar cells.

Figure 1. View of the crystal structures of (a) cubic diamond Si, Si (I), and (b) cubic Si(III) or BC8 (c*I*16).

Creating exotic allotropes of group 14 elements has been a matter of intense research among the scientific community for their importance in science and technology.[1,2] It is well-known that carbon exists in at least two different allotropic forms (diamond and graphite). Similarly, it has been shown that different polymorphs of Si and Ge exist.[1] In particular for silicon, the thermodynamically stable structure is the cubic diamond structure, also referred as Si (I), and is shown in Figure 1a.[2−5] This structure can be described as interconnected layers made up of hexagonal rings of Si in the chair conformation. There are other allotropes of Si such as the so-called BC8 or Si (III) phase, which is a high-pressure metastable state of Si having a body-centered cubic structure (Figure 1b).[6−8] In the BC8 structure, the hexagonal rings of Si are in the twisted boat conformation. This requires only a slight distortion of the Si tetrahedron without much change in interatomic distance (Figure b). The twisted boat conformation results in greater density compared with the diamond cubic structure, and the BC8 phase is a metastable high pressure form of Si. Though Si retains the diamond structure upon compression to ∼11.7 GPa, several other metallic forms have been discovered at higher pressure such as β-Sn or Si (II) (above ∼11.7 GPa) and a hexagonal phase or Si (V) (13−16 GPa).[4,6] However, on release of pressure from the metallic β-Sn form, it does not revert back to Si (I) but changes to several other metastable forms. One of these is the metastable structure, Si (III)/BC8. These phases have been realized via
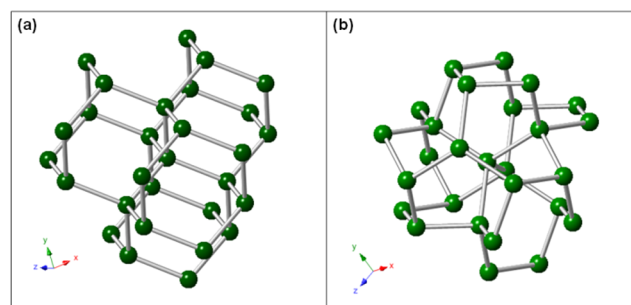
high-pressure techniques like femtosecond laser pulses[9] or in a hydraulic press.[3]

New polymorphs of various phases have been discovered as nanomaterials via colloidal routes.[10−12] It has been recognized that both energetics and mechanism of formation are important for accessing the metastable phases via colloidal chemistry.[13] For example, iron oxide polymorphs were synthesized via epoxide precipitation approach, and by changing the pH of the solution different polymorphs (magnetite, goethite, and lepidocrocite NPs) were formed.[11] In another example, Pan et al. have shown that Cu−In−S ternary phases could be synthesized in either the zincblende or wurtzite structures by changing the capping agent. This was the first example of zincblende and wurtzite structures for Cu−In−S via a solution route; the usual structure is tetragonal $CuInS_2$.[12]

To date, while there has been speculation concerning exotic forms of Si that might be accessible in NP form,[2] there is no evidence that they can be prepared by colloidal routes. Density functional and many-body perturbation theory calculations of Si NPs with BC8 core structure indicate that the BC8 Si NPs may exhibit significantly lower optical gaps and multiple exciton generation (MEG) thresholds than diamond structured Si.[2] Various routes such as reduction of silicon halides ($SiCl_4$) with sodium naphthalide,[14−18] oxidation of metal silicides with halogens[5] and ammonium bromide,[19,20] and metathesis reaction[21,22] between silicon halides and metal silicides have been reported to provide Si NPs in the diamond cubic structure phase as indicated by transmission electron microscopy (TEM) images and selected area electron diffraction (SAED).

Powder X-ray diffraction (PXRD) characterization of as-made colloidal Si NPs has not been reported to date. This is because either the as-made amounts are too small or the crystallite size is so small that they appear to be amorphous by

PXRD. The diffraction patterns, after heating to temperatures of 650 °C and above, show the cubic diamond structure of Si.[20,23,24]

This paper presents a new colloidal route to Si NPs with the cubic Si(III) or BC8 structure. The NPs are precipitated from solution and characterized by TEM, energy dispersive spectroscopy (EDS), SAED, and PXRD. Additionally, Raman spectroscopy, FT-IR, and photoluminescence (PL) properties of these materials will be presented and discussed.

In a typical Si NPs synthesis, 1 mmol of SiI_4 is mixed together in dioctylether (DOE) and heated to 170 °C. The reducing agent (3.75 mmol) n-butyllithium is injected, and after 10 min of stirring, 1-octanol (purged 1 h with argon) is added. The reaction mixture is further heated to 280 °C and stirred for an additional 72 h. The color of the solution changed from yellow to dark brown. The particles are isolated with hexane as the solvent and methanol as the antisolvent in a glovebox. After centrifugation, a brown precipitate is obtained. The precipitate is further dispersed in toluene and stored in glovebox for further use. It should be noted that with 1 mmol (0.535 g) of SiI_4, 28 mg of Si is expected with 100% yield, but the amount of precipitate obtained was ~6−10 mg (% yield = 22−35). In order to obtain sufficient quantities of the precipitate (so as to perform further studies), 2 mmol or more of Si precursor was used. Similar experiment was also performed using 1,2-hexadecanediol (HDD) as the capping agent instead of 1-octanol. In this case after injection of HDD the solution mixture was stirred for 30 min (at 200 °C) followed by precipitation with hexane and methanol.

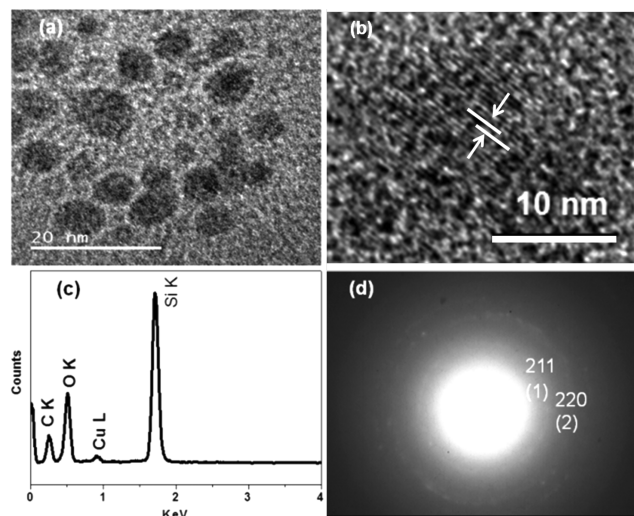The electron microscopy characterization is provided in Figure 2. As observed by the micrograph image, the octanol

Figure 2. (a) TEM of the Si NPs dispersed in toluene; (b) HRTEM of the NPs showing 220 plane; and (c) EDS and (d) SAED of the NPs.

capped NPs are quasi-spherical in shape with an average particle size of 5.5 ± 1.1 nm. The semiquantitative elemental analysis (EDS) shows that the predominant peak is the Si K peak. The O, C, and Cu K peaks are also apparent, consistent with the ligand and/or the grid. The HRTEM image confirms the crystallinity of the NPs where the lattice plane corresponds to the d-spacing of cubic BC8 Si (2.23 Å) giving the (220) plane. Additional measured lattice fringes along with their hkl planes from PDF no. 17-0901 database are reported in (Table S1 (SI)). Based on the lattice fringes that were measured, the

NPs crystallize in the cubic BC8 structure. The SAED pattern is also consistent with the BC8 structure of Si which is shown in (Table S2 (SI)). For the HDD capped NPs the TEM image obtained also showed quasi-spherical NPs with an average particle size of 5.0 ± 0.9 nm (Supporting Information, SI). The EDS shows that the predominant peak is the Si K peak. The diffraction spots obtained from the SAED are also consistent with the BC8 phase of Si (SI).

In order to further investigate the structure, the PXRD pattern of the precipitated octanol capped NPs was collected. The PXRD patterns were recorded on a BRUKER model D8 diffractometer in Bragg−Brentano reflection geometry with $CuK\alpha$ radiation (λ = 1.5418 Å). The experiment was carried out in the step mode with a fixed time of 4 s and a step size of 0.0194° for 2θ = 20−80° at room temperature in air. Figure 3a
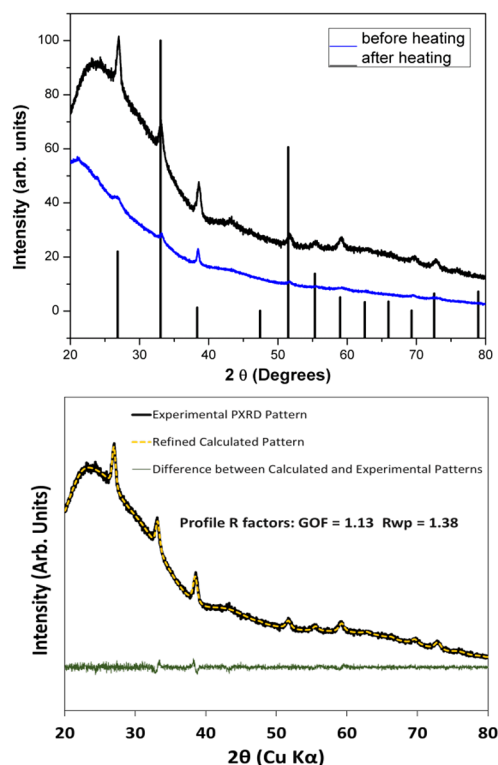

Figure 3. (a) PXRD of the precipitate before and after annealing which corresponds to cubic BC8 structure (PDF no. 17-0901). (b) PXRD pattern and whole profile refinement (LeBail method) of the annealed Si NPs.

shows the PXRD patterns of the precipitate, as-made and annealed at 650 °C for 2 h in a tube furnace under argon. The diffraction patterns were best fit with the Si (III) or BC8 crystal structure (Pearson symbol cI16).[3] As mentioned above, the reported PXRD patterns of Si NP prepared by other colloidal routes show the cubic diamond structure of Si only after heating to 650 °C.[20,23,24] Therefore, it is surprising that this synthetic route results in the BC8 phase and not cubic diamond (the PDF for the cubic Si diamond form is shown in the SI). In this route the surface linkage is through an oxide bond (shown by FTIR, SI), and this, along with the high temperature of the solution, may stabilize the BC8 structure. The as-made NPs show broad peaks with very weak intensities but still are best identified as the high-pressure cubic form of the BC8 structure shown in Figure 1b. After annealing, the peaks become more

intense as the samples became more concentrated and the ligand is removed (Figure 3b). Representative pattern of the annealed Si NPs, shown in black, is presented in Figure 3b on which the corresponding refined theoretical pattern, shown in yellow, is overlaid, and the difference profile is also shown below. The theoretical powder pattern calculated on the basis of the known crystalline phase of BC8 structure obtained from the ICSD database was refined by the Le Bail method using the whole profile matching method within JANA 2006. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. Good agreement between the observed and computed reflections, as demonstrated by small GOF and low Rwp values, provides a valuable indication that the high pressure cubic form of Si is synthesized, also consistent with SAED data presented in Table S3. So, these results suggest that the Si NPs with BC8 crystal structure, which is known as high-pressure cubic Si, are formed at ambient pressure and temperature of 280 °C. Annealing process can further enhance the crystallinity of the sample confirmed by increased peak intensities in the PXRD pattern. The values for the unit cell parameters and profile matching refinement are summarized in the Table S3. LeBail refinements for unit cell parameters resulted in smaller unit cell parameters compared to the previous studies on the bulk Si BC8 structure[3] which can be attributed to the effective surface tension of the NPs.[3,13]

The PXRD pattern of the as-made HDD capped Si NPs showed a featureless pattern suggesting amorphous peaks or less concentrated samples. When heated to 650 °C in a tube furnace under the flow of argon for 2 h the peaks became intense similar to the octanol capped NPs, but along with the Si peaks, HDD also crystallized, complicating the interpretation (SI), so was not pursued further.

Raman spectrum (Figure 4) of the octanoxide capped was collected using a Reinshaw RM1000 laser Raman microscope
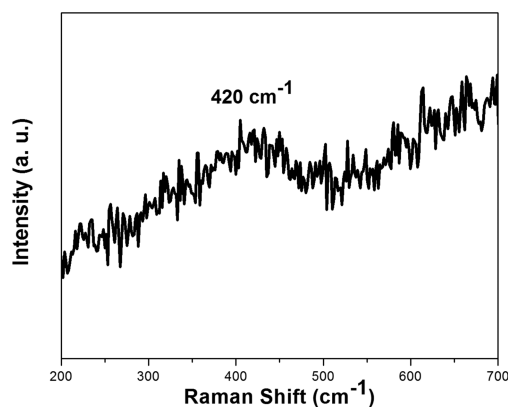

Figure 4. Raman spectrum of the precipitate obtained from the annealed octanol capped NPs.

with a motorized stage. The spectrum showed a weak intensity peak centered around 420 cm^{-1} which is similar to what is reported in literature for BC8 Si. For Si−I (diamond) the Raman peak for Si−Si is assigned to a strong stretching mode at 520 cm^{-1}. But the Si−Si mode in Si−III (BC8) should be very weak because of the distortion of the tetrahedron consistent with what is observed in Figure 4.[1] Although these samples clearly contain Si, the strong stretch at 520 cm^{-1} for Si−I was not detected in the sample. This suggests that there is little or no diamond cubic structured phase present. The Raman peaks were observed in the annealed sample as the annealed samples

were more concentrated, but unfortunately due to the weak intensity of the signal it was very difficult to observe any peak from the as made samples.

The optical properties of the BC8 structure were measured with the UV−vis spectrophotometer which extends from near IR to visible region (300−1600 nm, Figure 5). It is observed
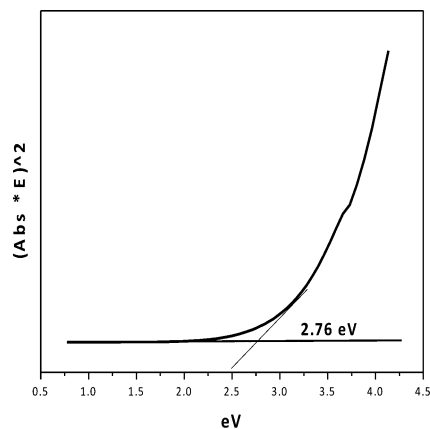

Figure 5. Tauc plot of the precipitate of octanol capped Si NPs.

that the sample mostly absorbs in the visible region of the spectra. In order to calculate the band gap of the octanol capped NPs, Tauc plot was employed $(\alpha h \nu)^2 = B(h\nu - E_g)$ where α = absorption coefficient, h = Planck's constant, ν = frequency, B = constant, and E_g = band gap of the material. Employing this equation it was noted that the E_g of the octanol capped NPs was 2.76 eV. According to theoretical calculations for the BC8 Si structure as a NP of diameter 4−8 nm, the E_g should be closer to 1.37 eV. A photoluminescence spectrum was also taken with the help of fluoromax-P luminescence spectrophotometer. The maximum intense emission wavelength in the PL spectra was centered at 425 nm at an excitation wavelength of 360 nm and shows blue luminescence when the sample in toluene was irradiated with a hand-held UV-lamp (as shown in Figure S5 (SI)). The intensity is similar to what is reported earlier in literature for Si NPs prepared by reduction. Typically, Si NPs prepared by colloidal routes show blue rather than red luminescence. The origin of this blue luminescence is still controversial, but recently it has been shown that the blue PL may be ascribed to N or impurity defect sites.[25] The blue emission observed for these NPs could be due either to defects in the structure or to N impurity as mentioned in the literature.

In conclusion, we have synthesized a metastable phase of Si in NP form via a colloidal reduction route for the first time. The TEM, EDS, and PXRD are consistent with the formation of the Si (III)/BC8 phase for Si. The Raman spectroscopy also supports the assignment to the BC8 structure. The optical properties suggest a higher band gap than expected for this structure,[2] suggesting the possibility of defects or N in the structure.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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