FAST TRACK COMMUNICATION

Silicon sheets by redox assisted chemical exfoliation

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Abstract

In this paper, we report the direct chemical synthesis of silicon sheets in gram-scale quantities by chemical exfoliation of pre-processed calcium disilicide (CaSi$_2$). We have used a combination of x-ray photoelectron spectroscopy, transmission electron microscopy and energy-dispersive x-ray spectroscopy to characterize the obtained silicon sheets. We found that the clean and crystalline silicon sheets show a two-dimensional hexagonal graphitic structure.

(Some figures may appear in colour only in the online journal)
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relativistic particles [10–13]. Therefore, all the expectations associated with graphene, such as high-speed electronic nanometric devices based on ballistic transport at room temperature, could be transferred to this new silicon material with the advantage of being compatible with existing semiconductor devices. Silicene has been grown by epitaxy on silver [14–18], gold [19] and Iridium [20] surfaces under ultra high vacuum (UHV) conditions. It is clear, however, that studying and understanding the properties of silicene, and the consequent development of silicene-based semiconducting devices, requires either the growth of silicene on insulating materials, or the preparation of bulk silicene by chemical methods.

In this paper we report the direct chemical synthesis of silicon sheets in gram-scale quantities by redox assisted chemical exfoliation (RACE) of calcium disilicide (CaSi$_2$). The latter consists of alternating Ca layers and corrugated Si(111) planes as shown in figure 1.

Silicene with a honeycomb graphene-like structure has been observed recently by scanning tunneling microscopy (STM) on Ag(110) and on Ag(111) surfaces [14, 15]. Silicene formation has also been studied on Au(110) [19], Ir(111) [20] and on ZrB$_2$ [21] surfaces. Furthermore, silicene nanoribbons deposited on a Ag(110) surface have shown reduced reactivity to oxygen compared to a Si(111) layer [22] which makes them promising candidates for stable devices. So far, these silicon structures have been grown using epitaxial growth techniques under UHV. However, chemical processes may provide an alternative route to large-scale synthesis of 2D silicon nanomaterials under production conditions. To the best of our knowledge, only a few investigations have been performed to synthesize 2D silicon structures [23]. From a chemical point of view, it is well known that silicon forms a variety of stable binary Zintl compounds$^{10}$ in which silicon forms the anionic part of the structure and alkali, alkaline earth or lanthanide metals form the cationic part [25–27]. Among the Zintl silicides, only calcium disilicide (CaSi$_2$) has a structure of interconnected Si$_6$ rings forming anionic 2D silicon puckered sheets of (Si$_2$)$_2$ held together by Ca$^{2+}$ that form planar monolayers (figure 1). The covalent structure of the silicide layers is stable and remarkably flexible [28–30] and can be chemically modified by oxidation, leading to removal of the intercalated metal ions. Using these experimental observations, a synthesis of a 2D Si backbone of siloxene nanosheets (Si$_6$H$_3$(OH)$_3$) was reported in an earlier publication [23]. Unfortunately the silicon skeleton was partially oxidized [31]. Nakano et al reported the synthesis of Mg-doped silicon sheets—capped with oxygen—by exfoliation of Mg-doped CaSi$_2$ [32]. Despite these studies, the chemical synthesis of pure silicon sheets has not yet been reported. In the present study, we report results on the synthesis of silicon sheets by chemical exfoliation of (Si$_2$)$_2$ from CaSi$_2$ using a modified procedure published by Nakano et al [30]. We call this method redox assisted chemical exfoliation (RACE). Let us recall that CaSi$_2$ is an ionic (Ca$^{2+}$ (Si$_2$)$_2$) material, and the reduction of the charge on the (negatively charged) silicon layers is an important step in order to diminish the strong electrostatic interaction between the Ca$^{2+}$ and (Si$_2$)$_2$ layers [32].

A 150-ml Schlenk tube$^{11}$ with a magnetic stirring bar is charged with 2.66 mmol CaSi$_2$ (Aldrich, Ca: 30–33% and Si: 60–62%) (255.1 mg) and 5.32 mmol of metallic potassium (Merck, 96%) (208 mg). The tube is purged with N$_2$ three times and heated under a pressure of 0.01 mbar at 160°C for 5 h. After cooling to room temperature (RT), a degassed solution of 10 g isopropylamine hydrochloride (iPA HCl) in 50 ml of ethanol is gradually added under nitrogen until the amalgam is obtained. The mixture is degassed by three vacuum-filling nitrogen cycles and magnetically stirred at RT

$^{11}$Schlenk tube is ‘glass laboratory equipment’ designed for the handling of compounds that are air sensitive.
for 24 h to form a green-brown precipitate of fine particles. Subsequently 50 ml of degassed water was added to the tube, and the mixture was allowed to decant for a period of 30–40 min to form a black deposit at the bottom of the Schlenk tube which was found to be unreacted CaSi$_2$ as confirmed by powder x-ray diffraction. The floating particles (less dense than water) are recovered by filtration and the solid is washed with cold water 3 times to remove any formed chloride salts. The green-brown solid is dried at RT under vacuum for 4 h yielding silicon sheets corresponding to 20% of the used CaSi$_2$.

In the original work by Nakano et al [32] Mg-doped CaSi$_2$ (CaSi$_{1.85}$Mg$_{0.15}$) was used as a precursor to the chemical synthesis of silicon sheets. They prepared CaSi$_{1.85}$Mg$_{0.15}$ by melting a mixture of CaSi, Si, and Mg; then the material obtained was treated in a solution of propylamine hydrochloride (PA·HCl), resulting in the de-intercalation of Ca$^{2+}$ ions and the formation a light-brown suspension containing silicon nanosheets (SNSs). The authors proposed the following mechanism for the exfoliation process: (1) oxidation of CaSi$_{1.85}$Mg$_{0.15}$ initiated by the oxidation of Ca atoms with PA·HCl, accompanied by the liberation of PA; (2) the presumably very reactive Mg-doped Si$_6$H$_6$ obtained is readily oxidized by water to form gaseous hydrogen; (3) Mg-doped layered silicon with capping oxygen atoms is exfoliated by reaction with the aqueous solution of PA. This mechanism helped us to design and propose the following scheme for the present exfoliation. In our case the exfoliation occurs in the following steps.

1. Diffusion of potassium (K) in CaSi$_2$ at 160°C leads to the formation of the K$_2$Ca$_{1-x}$Si$_{2-x}$ phase and a small amount of KSi and Ca metal driven by the reduction of some Ca$^{2+}$ by K, as shown in the following chemical equation (1):

$$\text{CaSi}_2 + 3x\text{K} \rightarrow \text{K}_2\text{Ca}_{1-x}\text{Si}_{2-x} + x\text{KSi} + x\text{Ca} \quad (1)$$

2. The treatment of the mixture obtained (amalgam) by an ethanolic solution of isopropylamine hydrochloride (iPA·HCl) leads to the formation of Si nanosheets (SNSs). These steps can be summarized by the following chemical equations:

$$\text{K}_2\text{Ca}_{1-x}\text{Si}_{2-x} + 2\text{iPA} \cdot \text{HCl} \rightarrow 2\text{xKCl}$$

$$+ (1 - x)\text{CaCl}_2 + (2 - x)\text{Si(SNSs)}$$

$$+ 2\text{iPA} + \text{H}_2 \quad (2)$$

$$\text{Ca} + 2\text{iPA} \cdot \text{HCl} \rightarrow \text{CaCl}_2 + 2\text{iPA} + \text{H}_2$$

$$\quad (3)$$

The excess potassium reacts with iPA·HCl to release H$_2$ as follows:

$$\text{K} + \text{iPA} \cdot \text{HCl} \rightarrow \text{KCl} + 2\text{iPA} + 1/2\text{H}_2 \quad (4)$$

We have analyzed the synthesized sheets by x-ray photoemission spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM) and energy-dispersive x-ray spectroscopy (EDX). The Si 2p core level was probed by XPS at the SOLEIL synchrotron radiation facility on the TEMPO beam line, at binding energies (BEs) of ~100 eV (figure 2).

Note that within the precision of the instrument, the Si binding energies are very close to those of bulk silicon [31].
As a matter of fact, the XPS measurements show that the synthesized sheets contain almost exclusively Si atoms. In addition, to check the oxidation trace in the silicon sheets we have performed energy-dispersive x-ray spectroscopy (EDX) experiments. Figure 3 shows different spectra corresponding to the analysis of different grains. Figure 3(a) corresponds to the starting CaSi$_2$ powder showing both Si and Ca peaks. Figures 3(b) and (c) correspond to grains of silicon sheets indicating that the Ca atoms have been completely removed. However in figure 3(b) we observe a small trace of oxygen, which is due to exposure of the powder to air. Let us note that the observed Al peak on all figures is due the sample holder, which is made from aluminum.

In order to provide further insight into the atomic structure of the prepared silicon sheets, we have performed HR-TEM measurements. Figure 4(a) reveals that the synthesized silicon product consists of multiple silicon sheets. At high resolution, the silicon sheets are highly ordered (figure 4(b)). The diffraction pattern in figure 4(c) shows a hexagonal spot arrangement. This provides clear evidence that the silicon sheets are well ordered and crystalline.

This hexagonal pattern originates either from a quasi-two-dimensional hexagonal lattice directly, like that of silicene, graphene and carbon nanotubes, or from a (111) oriented sheet (puckered layer) of a Si bulk diamond lattice. For the hexagonal system, the observed spots correspond to the four (100) and the two (110) reflections. The first spot of the diffraction pattern, located at $3.49 \pm 0.20$ nm$^{-1}$ from the center, gives an interlayer spacing ($d_{100}$ or $d_{110}$) of $0.286 \pm 0.016$ nm in the direct lattice. From the distance $d_{100}$ (or $d_{110}$), equal to $a_{\text{hex}} \times \sqrt{3}/2$ (where $a_{\text{hex}}$ is the 2D hexagonal lattice constant, see figure 1(b)), we deduce a value of $a_{\text{hex}}$ equal to $0.330 \pm 0.018$ nm. This value is smaller than the $0.38$ nm corresponding to the hexagonal lattice constant of the (111) oriented layers of a silicon diamond lattice. Hence the structure of the synthesized Si sheets cannot correspond to the (111) oriented layer of Si diamond lattice. Therefore, these silicon sheets may correspond to a 2D honeycomb Si lattice stacked in planes with a surface lattice constant $a_{\text{hex}} = 0.330 \pm 0.018$ nm, corresponding to a distance between the first Si atom neighbors of 0.19 nm. Let us recall that all the previous studies report that the silicene is corrugated [15, 17, 20, 34–36] with a buckling between 0.04 and 0.12 nm [11, 33], resulting in a projected distance (in the plane of the hexagons) as low as 0.19 nm. Hence, the first neighbor Si–Si distance in the present study is close to those reported for silicene sheets (0.20, 0.22, 0.25 nm) [15, 17, 34].

In conclusion, we have synthesized extended silicon sheets by a simple room temperature procedure called redox assisted chemical exfoliation of calcium disilicide (CaSi$_2$). The data show clearly that the synthesized Si sheets do not correspond to the (111) oriented layer of Si diamond lattice; instead they have a hexagonal graphitic-like structure resembling that of silicene. In order to increase the size of
these sheets, an improved synthesis is under investigation using an appropriate stabilizer, which will prevent the sheets aggregating.

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