# Synthesis of Si Nanosheet Bundles by Extraction of Ca Atoms from CaSi<sub>2</sub> Powders by Inositol Hexakisphosphate Solution

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# Abstract

Si nanosheet bundles were synthesized by Ca atom extraction from CaSi<sub>2</sub> powders using inositol hexakisphosphate, which is known as a phytate for metal storage found in cereals and grains. The raw CaSi<sub>2</sub> powders were simply immersed in a diluted inositol hexakisphosphate solution, then dried. The structural, optical and electronic properties of the Si nanosheets were examined.

# 1. Introduction

Low-dimensional materials have attracted much interest because of their enhanced or modified optical, electronic and mechanical properties compared to those of bulk materials. The free standing Si nanosheets, including Silicene, Siloxane, Polysilane and other Si two dimensional (2D) layered structures, have been synthesized.

The formation of Siloxene by Ca extraction from  $CaSi_2$  by electrochemical methods in solutions was reported. In addition, two dimensional (2D) "active silicon" or 2D silicon sheets were also synthesized by the reaction between  $CaSi_2$  and pure  $Cl_2$  or metal-chlorides.

On the other hand, inositol hexakisphosphate (IP6)  $C_6H_{18}O_{24}P_6$ , which is known as a phytate for metal storage found in cereals and grains. The active reactions with the divalent metal ions to form phytate complexes were reported [1]. Thus, it is expected that the metallic atoms can be extracted from the silicides using IP6 by its strong chelate effect. In this study, the synthesis of Si nanosheets by extraction of the Ca atoms from CaSi<sub>2</sub> powders using IP6 is reported. In addition, the structural, optical and electronic properties of the Si nanosheets were examined.

# 2. Experimental procedure

Commercially available  $CaSi_2$  powders are used as source materials. The powders were immersed typically in a 20% diluted IP6 solution at 40 °C for 1 h. then dried. The structural, optical and electronic properties of the nanosheets were characterized by XRD, SEM, TEM, FTIR and XPS.

## 3. Results and discussion

Figure 1(a) shows a SEM image of raw  $CaSi_2$  powders, which consist of particles with a nonuniform size up to hundreds of micrometers. The  $CaSi_2$  powder was dispersed into the dilute 20% IP6 solution at 40 °C for 1h. After the treatment, synthesized products are shown in Fig. 1(b) and (c). Nanosheet bundle structures were synthesized and the 2D sheets in the structures could be clearly seen with thicknesses of 50 to 200 nm and the width up to hundreds of micrometers.



Fig. 1 SEM images of (a) raw  $CaSi_2$  powders, (b) Si nanosheet bundle structure treated by IP6 solution, and (c) enlarged cross-sectional view of the Si nanosheet bundle.

Figure 2 show the XRD spectra of Si nanosheet bundles formed by the reaction of  $CaSi_2$  powders with IP6 solution. The XRD spectrum of raw  $CaSi_2$  powder is also shown as a comparison. The raw  $CaSi_2$  powder includes two trigonal rhombohedral modications or polytypes (tr3 and tr6). As shown in Fig. 1(a), after the treatment for 1h, new XRD peaks appear at 28.4 and 56.2°, corresponding to the crystalline Si(111) and Si(311) peaks. However, some peaks due to the CaSi<sub>2</sub> remains and a small broad peak at 20-30° due to the amorphous phase appears. Figure 1(c) shows the spectrum of the Si nanosheet bundle formed by the 30 % IP6 solution for 1 h. Only sharp peaks attributed to crystalline Si were observed, with the larger broad amorphous peak.



Fig. 2 XRD spectra of the nanosheet bundles synthesized by (a) 20% IP6 solution for 1h, (b) 20% IP6 solution for 10h and (c) 30% IP6 solution for 10h. The XRD spectrum of raw CaSi<sub>2</sub> powders is also shown.



Fig. 3 (a), (b) Typical TEM images of the Si nanosheet bundle structure viewed perpendicular and parallel to the surface, respectively. (c) TEM image of nanosheet exfoliated from the structure. (d) HRTEM image of the Si nanosheet, and the inset shows its FFT pattern.

A series of TEM images of the Si nanosheet bundle structures and nanohseets synthesized by 20% IP6 solution for 1h are shown in Fig. 3. The nanostructure consists of multiple sheets, which are overlapped clearly. The thickness of sheets is about a few tens of nanometers, estimated from Fig. 3(b). Figure 3(c) shows one piece of nanosheets exfoliated from the bundle structure. The HRTEM image and the corresponding Fast Fourier Transformation (FFT) pattern are shown in Fig. 3(d). According to the lattice image, the plane spacing of 0.19nm corresponds to Si(20 $\overline{2}$ ). The plane spacings of 0.32nm are due to so-called 1/3{422} spots. The surface of the nanosheets is identified as Si {111}.

Figure 4 shows the FTIR spectrum of the nanosheet bundles treated with 20% IP6 solution for 1h. The absorption peaks obtained at 443, 715, 831 and 1064 cm<sup>-1</sup>, are corresponding to bending bond of network Si-O-Si, symmetric stretching of Si-O-Si, stretching of Si-OH and antisymmetric stretching of Si-O-Si, respectively. The bonding of silicon to oxygen was confirmed. From the spectrum, the peak at 2148cm<sup>-1</sup>, originating from the OSi<sub>2</sub> $\equiv$ Si-H bond, implies that the presence of Si planes. The presence of the band at 2250 cm<sup>-1</sup> and 3400 cm<sup>-1</sup>, attributed to the O<sub>3</sub> $\equiv$ Si-H and – OH bonds, suggesting that the edges and the majority of the surface area of the nanosheets may also have been oxidized and hydroxylated.



Fig. 4 FTIR spectrum of Si nanosheet bundle synthesized with  $CaSi_2$  powder treated by 20% IP6 solution for 1h.



Fig. 5 (a) XPS wide scan spectrum of Si nanosheet bundle treated by 20% IP6 solution for 1h. (b) high resolution XPS spectra for the Si 2p peaks of the Si nanosheets and raw  $CaSi_2$  powders.

In Fig. 5, XPS spectrum of the Si nanosheet bundle is shown. The XPS binding energy of Si 2p peaks are shown in Fig. 5(b). The peaks at 104 eV and 99eV are attributed to SiO<sub>2</sub> (Si<sup>4+</sup>) and bulk Si (Si<sup>0</sup>), respectively. The binding energy between 100 eV to 103 eV for Si are 100.6 eV for Si<sup>1+</sup>, 101.6 eV for Si<sup>2+</sup> and 102.7 eV for Si<sup>3+</sup>. No Si<sup>0</sup> peak was distributed on spectrum of raw CaSi<sub>2</sub>. The results indicate that significant amounts of intermediate Si states, such as Si<sup>1+</sup>, Si<sup>2+</sup> and Si<sup>3+</sup>, remains, which is due to the formation of oxygen passivated layers or other oxidation products. The clear shoulder peak around 99eV is attributed to Si<sup>0</sup>.

#### 4. Conclusions

Si nanosheet bundles were synthesized by Ca atom extraction from  $CaSi_2$  powders using IP6. The  $CaSi_2$  powders were simply immersed in diluted IP6 solution, then dried. The growth process is extremely simple, useful and practical for the applications to large area or large volume devices. The morphological and structural modification technique by IP6 with using additional metallic materials is proposed.

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#### References

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