Synthesis of Si-based Nanostructures by Extraction of Metallic Atoms from Silicides by Inositol Hexakisphosphate

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Abstract
Si-based nanostructures were synthesized by metallic atom extraction from silicides using inositol hexakisphosphate, which is known as a phytate for metal storage found in cereals and grains. The silicide bulk or powders were simply immersed in a diluted inositol hexakisphosphate solution, then dried. Si-based nanosheets and three dimensional network structure with SiOx were obtained. The structural property of the nanostructures was 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 and other Si sheet two dimensional (2D) layered structures, have been synthesized.

The formation of Si nanosheets by Ca extraction from CaSi2 by electrochemical methods in solutions, and the synthesis of Siloxene were reported. On the other hand, 2D “active silicon” or 2D silicon sheets were synthesized by the reaction between CaSi2 and pure Cl2 or metal-chlorides.

On the other hand, inositol hexakisphosphate (IP6) C6H11O12P6, which is known as a phytate for metal storage found in cereals and grains, is the principal storage form of phosphorus in many plant tissues, especially bran and seeds. The preparations of the metal phytate complexes were reported [1]. In addition, the active reactions with the divalent metal ions to form phytate complexes were reported [2]. 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-based nanostructures by extraction of the metallic atoms from silicide bulk or powders using IP6 is reported. In addition, the structural properties of the nanoparticles were examined.

2. Experimental procedure
Commercially available silicide bulk or powders are used as source materials. The silicide bulk or powders were immersed in a 20% diluted IP6 solution at 40 °C for 60 min. then dried. The morphological and structural properties of the nanostructures were characterized.

3. Results and discussion
Figure 1 shows SEM images of nanostructures synthesized using Mg2Si, SrSi2 and BaSi2 source materials. In lower scale magnification images, particles with the size of several tenth of micrometers are observed. In enlarged magnification images, three dimensional network structures and two dimensional sheets are observed for Mg2Si and SrSi2 source materials, respectively. For the case of BaSi2 source material, both of two dimensional sheet and three dimensional network structures were formed.
Figure 2 shows TEM, HRTEM images and corresponding FFT pattern of the nanosheet synthesized from the BaSi$_2$ source material. The results revealed that the Si nanosheets are formed, and the nanosheet surface is Si(111).

Figure 3 shows STEM image and corresponding EDS mappings of the nanonetwork synthesized from the BaSi$_2$ source material. The three dimensional nanonetwork structures are obvious. The EDS results reveal that the nanostructures consist of silicon and oxygen. Small amount of phosphorus was found and the Barium was hardly detected. It is confirmed that Ba atoms were extracted from BaSi$_2$, to form Si-based nanonetwork with SiO$_x$.

Figure 4 shows cathode luminescence spectra of the nanostructures synthesized using Mg$_2$Si, SrSi$_2$, and BaSi$_2$ source materials. The UV or blue emission has been ascribed to a defective oxide phase present on the surface of the nanocrystals [3]. These impurities or defects, most likely SiO$_2$ or Si-O-H bonds, may have been formed during the fabrication process or during subsequent storage in ambient air. The luminescence band observed at $\sim 620$ nm is believed to be due to quantum confinement effects in the silicon particles [4]. It is found that the luminescence peaks due to SiO$_2$ but also due to Si is observed. The electronic, optical and thermal properties of the nanosheets have not been clarified at this moment. The difference of functional properties between the Si/SiO$_2$ obtained here and a common Si/SiO$_2$ bulk crystal is not known. However, new functional properties for the structurally modified crystals would be expected.

![BaSi$_2$](image1)

![STEM images](image2)

![EDS mappings](image3)

![Cathode luminescence spectra](image4)

It is demonstrated that metallic atoms were extracted from the silicides by the strong chelate effect of IP6, and the Si-based nanostructures with SiO$_2$ were formed. The IP6 is abundant and safe. It is known for metal storage in the environmental or biomaterials fields. It is expected that other chelating agents can be also used to synthesize new nanomaterials. In addition, nanoscale morphological and structural control of the materials would be also possible by the appropriate choice of the silicide crystalline structure.

4. Conclusion

Si-based nanostructures were synthesized by metallic atom extraction from silicides using inositol hexakisphosphate (IP6), which is known as a phytate for metal storage found in cereals and grains. The silicide bulk or powders were simply immersed in diluted IP6 solution, then dried. The growth process is extremely simple, useful and practical. The morphological and structural modification technique by IP6 and other chelating agents with using additional metallic materials is proposed.

References