Synthesis of CaF₂ Nanostructures from Calcium Silicide Powders in Diluted Aqueous HF Solution

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CaF₂ nanostructures were synthesized from Ca-silicide powders by a diluted aqueous HF treatment. Commercially-available CaSi₂ crystal powders and calcium silicide powders prepared by mechanical alloying were used as the source materials, and CaF₂ nanosheet bundles and nanobunches of the CaF₂ nanoparticles were obtained, respectively. The morphological property of the resulting CaF₂ nanostructures was characterized by electron microscopy. It was found that the morphology of the resulting products depended on the starting materials. In addition, the growth mechanism of the CaF₂ nanostructures was discussed from a topological synthesis point of view.

1. Introduction

Low-dimensional materials have attracted much interest because of their enhanced or modified optical, electronic and mechanical properties compared to those of the bulk materials. CaF₂ is widely known as one of the excellent optical materials, and its thermoluminescent property has been investigated [1–4]. Recently, CaF₂ nanoparticles (NPs) were applied in theranostics for diagnostic analysis, optical imaging, cell labeling, drug delivery and tumor therapy, as shown in Ref.5. In addition, dental applications of the CaF₂ NPs were reported [6]. Moreover, the anti-bacterial activity and cytotoxicity of CaF₂ NPs were investigated [7].

To synthesize nanostructures, the topological synthesis technique has been widely used. As one of the examples, CaSi₂ is used for the formation of a Si-based two-dimensional nanostructure [8]. The synthesis of CaF₂ nanosheets has been reported, but the product consists of CaF₂ in three morphologies: square or rectangular nanosheets, irregularly-shaped particles, and sparse square-shaped platelets. The platelets can be separated by centrifugation, but the nanosheets and nanoparticles remain mixed in the samples subjected to characterization and reactivity studies [9]. It has also been demonstrated that the morphology of the resultant products depends on the position and the bonding direction of the Si atoms in the initial crystals [10].

Multiple silicide phases, such as CaSi₂, Ca₃Si, CaSi, and Ca₃Si, exist in the Ca–Si system. CaSi₂ has a zintl phase, trigonal structure (CaSi₂-type) (R3m, No.166). In addition, it was reported that a calcium silicide prepared by mechanical alloying has a cubic structure, if it was prepared under the appropriate conditions described in the literature [11]. In this study, the synthesis of CaF₂ nanostructures was examined, and morphological control of the nanostructures was investigated from the view point of topological synthesis.
2. Experiments

Commercially-available (CA) CaSi$_2$ crystal powders (ca.1~10 µm, 2N, Kojundo Chemical Lab. Co., Ltd.) were dipped in an aqueous HF (~0.3, 3 mol/L) solution at room temperature for 5 to 60 min. After the products were filtered for about one hour, substances that remained on the filter paper (JIS P 3801 5C, α-cellulose, pore size 1µm) were dried at room temperature. Calcium silicide powders formed by a mechanical alloying (MA) procedure were also used as the starting materials. The powders were alloyed from fine Si powder (APS ≤ 50 nm, 98%) and Ca granules (2~4 mm, 2N). The Ca and Si powders were weighed in the molar ratio of Ca:Si=2:1. The powders and four 1/4 inch steel milling balls were placed in a steel vial under an argon atmosphere, then the vial was sealed by an O-ring. The milling was carried out using a SPEX 8000 vibratory mill for 50 h [11]. The milled powders were denoted as “MA-calcium silicide powder” in this paper, and were also treated in the HF solution by a 15 min dipping and subsequent filtration process.

The morphological and structural properties of the products were characterized by X-ray diffraction (XRD) measurements, field-emission scanning electron microscopy (FE-SEM) with energy dispersion spectroscopy (EDS), conventional transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) with Fast Fourier Transform (FFT). For the TEM sample preparation, the products were dispersed in a small amount of ethanol, then transferred onto a lacy-carbon-coated copper grid and dried.

3. Results and discussion

The structural and morphological properties of the CaF$_2$ product synthesized by the dipping and subsequent filtration treatment using the HF (3 mol/L) solution are described in this section as follows, except the result of the product shown in Fig.2(d). First, the products synthesized using the CA-CaSi$_2$ crystal powders and the MA-calcium silicide powders were examined by XRD measurements. For both cases, it was confirmed that the CaSi$_2$ phase still remained after a 5 min. dipping and subsequent filtration treatment, but after a 15 min. dipping and subsequent filtration treatment, the CA-CaSi$_2$ and MA-calcium silicides were decomposed as shown in Fig.1. The lattice parameter of CaF$_2$ (0.5462 nm) is well-matched with that of silicon (0.5431 nm), thus it is difficult to distinguish the diffraction peak corresponding to only CaF$_2$ [12,13]. It is necessary to identify the crystalline phase with the chemical distribution analysis as described later.

Fig. 1. XRD spectra of the HF-treated products synthesized from CA-CaSi$_2$ for (a) 5, and (b) 15 min dipping and subsequent filtration treatment, and (c) MA-Calcium silicide powders for a 15 min dipping and subsequent filtration treatment.
The morphology of the products synthesized using the CA-CaSi$_2$ powders is described. The products shown in Figs. 2(a)–(c) were synthesized from CA-CaSi$_2$ powders by a 15 min dipping and subsequent filtration treatment, which show features of the intermediate process of transforming from the CaSi$_2$ powders to nanosheets. It was found that the product showed a powder form, as shown in Fig. 2(a), and the powder was formed by a collection of nanosheets, as shown in Fig. 2(b). In the cross-sectional view TEM, the nanosheet bundle structure was clearly seen with a collection of nanosheets having a thickness of about 50 nm overlapping each other along with a void space in Fig. 2(c). To observe the initial stage of structural transformation from CaSi$_2$ crystals to CaF$_2$ nanostructures, the synthesis from the CA-CaSi$_2$ powders by a 15 min dipping and subsequent filtration treatment using the HF (0.3 mol/L) solution was examined, and the result is shown in Fig. 2(d) as a cross-sectional TEM image of the product. It was found that the powder was torn and split into the layers, and the CaF$_2$ were distributed between the exfoliated layers of the original powder.

Focusing on the nanosheet structures in the products synthesized from the CA-CaSi$_2$ powders for a 60 min dipping and subsequent filtration treatment using the HF solution (3 mol/L), the products are shown in Figs. 2(e)–(g). It was found that three types of nanosheets were mainly observed. The first one is a moderately facetted nanosheet shown in Fig. 2(e), which was identified as a CaF$_2$ nanosheet based on the EDS mappings and HRTEM observations described later. The second one is an unknown crumpled large nanosheet shown in Fig. 2(f). As shown in Fig. 2(g), the last one is the well-facetted Si nanosheets, which was identified using EDS mappings and HRTEM observations [14]. In this paper, further characterizations of the products focused on only one kind of nanosheet, as only shown in Fig. 2(e).

Fig. 2. (a) Low magnification, (b) enlarged SEM images, and (c) cross-sectional TEM image of the products synthesized from CA-CaSi$_2$ powders by the 15 min dipping and subsequent filtration treatment using the HF (3 mol/L) solution. (d) Cross-sectional TEM image of the product synthesized from CA-CaSi$_2$ powders by the 15 min dipping and subsequent filtration treatment using the HF (0.3 mol/L) solution. TEM images of three types of nanosheets; (e) moderately facetted CaF$_2$, (f) unknown crumpled, and (g) well-facetted Si nanosheets synthesized from CA-CaSi$_2$ powders with the 60 min dipping and subsequent filtration treatment using the HF (3 mol/L) solution.

As already described, the characterization of the chemical distribution is important in order to identify the crystalline phase. The EDS mapping of the products synthesized from the CA-CaSi$_2$ powders with the 15 min dipping and subsequent filtration treatment is shown in Fig. 3(a). It was confirmed that the Si atoms were extracted from the CA-CaSi$_2$ powder, and calcium fluoride was formed by the HF treatments. In the mappings, Si is slightly inhomogeneously distributed,
corresponding to the oxygen distribution. The chemical distribution of the nanosheets shown in Fig. 2(e) is also shown in Fig. 3(b). In the image, several small irregular-shaped species are also observed, which may be broken during the TEM sample preparation process. The formation of calcium fluoride is confirmed again in the range of the nanosheet size.

A detailed HRTEM observation was made for the nanosheets as shown by the arrows in Fig. 3(b), and the HRTEM images are shown in Fig. 4. The stepped structure of the nanosheet is clearly observed, as shown in Fig. 4(a). In Fig. 4(b), several domains connected to each other to form the sheet form are observed, which means that the nanosheet is polycrystalline. HRTEM image (Fig. 4(c)) and corresponding FFT pattern (Fig. 4(d)), taken in a part of the domain shown in Fig. 4(b), agrees with the lattice image and the ideal diffraction pattern of CaF$_2$ with the [101] observation direction. In the image, faint additional FFT spots were also observed by the formation of polycrystalline phases. Along with the EDS mappings, the nanosheet is identified as CaF$_2$, but the sheet is polycrystalline.

![Fig. 3.](image)

(a) SEM image and corresponding EDS mappings of the powder consisting of the calcium fluoride synthesized from the CA-CaSi$_2$ powders by the 15 min dipping and subsequent filtration treatment. (b) STEM images and corresponding EDS mappings of the calcium fluoride nanosheets synthesized from the CA-CaSi$_2$ powders by the 60 min dipping and subsequent filtration treatment.

![Fig. 4.](image)

(a)–(c) HRTEM images and corresponding FFT pattern of the calcium fluoride nanosheets synthesized from the CA-CaSi$_2$ powders by the 60 min dipping and subsequent filtration treatment.

In Ref. 9, the formation mechanism of the polycrystalline nanosheets is considered as follows: the fast formation of CaF$_2$ in the limited interlayer spaces [\(\sim 0.5 \text{ nm between } (\text{Si})_n\text{ sheets}\) accounts for the observed nanosheet morphology. Additionally, CaF$_2$ formation is templated between the silicon layers of the CaSi$_2$ as the fluoride ions first react with the interlayer calcium ions. After the CaF$_2$ formation is completed, there are no dangling bonds attaching CaF$_2$ to the silicide layers, and
the CaF$_2$ nanosheets are easily released as the silicide is consumed. Thus, both the confinement and templating direct the two-dimensional growth of CaF$_2$ in this system. On the other hand, the polycrystalline CaF$_2$ nanosheets with thicker layer thickness (around 50 nm or less) and wider area (order of sub-micro to micrometers) were obtained in this study. By comparing the results in this study with the growth phenomena of the CaF$_2$ nanosheets in the literature, it is considered that the two-dimensional growth of CaF$_2$ imperfectly takes place, presumably because of the higher reaction ratio of CaSi$_2$ with HF under the examined synthesis condition in this study. The CaF$_2$ crystals having sheet-like morphology were deposited, then, developed to free standing nanosheets after the original powder was decomposed. The polycrystalline deposition of the condensed CaF$_2$ layers leads the formation of the polycrystalline nanosheets. To improve the crystalline quality of the nanosheets, epitaxial or templating deposition of CaF$_2$ on the surface of the exfoliated layers is important. In addition, the formation of a biproduct of H$_2$SiF$_6$ or CaSiF$_6$ was also reported [9]. It should be pointed out to improve the crystalline quality of the nanosheets that the formation of biproducts of H$_2$SiF$_6$, CaSiF$_6$, and CaSiF$_6$·2H$_2$O would play important roles to form nanosheets of the CaF$_2$ crystal, because the precipitates obtained from the residual solution, in which these compounds would be included, were condensed in the sheet morphology [14]. Further investigation of the nanosheet synthesis technique to improve the quality of the nanosheets will be required.

Next, the morphology of the CaF$_2$ crystals prepared using the MA-calcium silicide was observed. It was found that the product had a powder form, and the powder was formed by a collection of smaller particles, which looks like sandstone, as shown in Figs.4(a) and (b). The TEM observation of part of the product scratched off the powder shows that a bunched structure was formed, and it consisted of nanoparticles with a diameter around 10 nm, as shown in Fig.4(c). The HRTEM image and the corresponding FFT pattern in Fig.4(d) revealed that the nanoparticles in the nanobunch showed that the CaF$_2$(111) planes of the domains were preferentially distributed along the directions shown by the red dotted arrows. The angles of 71° correspond to that between the CaF$_2$ (111) and (111) planes, and used as a visual guide. It also shows the superposition of the FFT patterns of CaF$_2$ denoted as CaF$_2$ 111, and those of the MA-calcium silicide shown as CS1 and CS2. The actual phase of the MA-calcium silicide has not been identified [11], thus, CS1 and CS2 are used to describe the patterns. It is considered that the nanoparticles were then formed, and the CaF$_2$(111) planes were distributed parallel to each other, presumably at the interface between two adjacent particles.

Fluorine atoms were diffused into the CaSi$_2$ crystals, then CaF$_2$ layers were formed in the crystals [15]. The formation of the CaF$_2$ layers was also reported for the use of CaGe$_2$ crystals [16]. The crystallographic symmetry of the CaSi$_2$ and CaGe$_2$ starting crystal was maintained even during the transformation from CaSi$_2$ to CaF$_2$ by the Si extraction and F incorporation processes. It was also confirmed that the Si atoms were extracted from the MA-calcium silicide powders and CaF$_2$ was formed by the HF treatments, as shown in the SEM images and corresponding EDS mappings of the powder consisting of the CaF$_2$ nanobunches or nanoparticles in Figs.5 and 6.

**Fig. 5.** (a) Low magnification and (b) enlarged SEM images, (c) TEM, and (d) HRTEM images and corresponding FFT pattern of the CaF$_2$ bunch of nanoparticles synthesized from the MA-calcium silicide powders by the HF treatment.
The morphological control of the CaF$_2$ nanostructure was demonstrated by the HF treatment of the appropriate Ca-silicide as the starting material. As the starting material, when the CA-CaSi$_2$ crystals were used, CaF$_2$ nanosheet bundles were formed. On the other hand, when MA-calcium silicide was used, CaF$_2$ nanobunches or nanoparticles were formed. It was reported that that MA-calcium silicide has a cubic phase structure, and showed a semiconducting property [11]. The difference in the crystalline structure of the starting materials affects the morphology of the final products. The characteristic morphology of each product of the CaF$_2$ nanostructures can be developed into applications that take advantage of each property as already mentioned. Further control of nanoscale morphological property would be possible for designing the nanoscale architectures.

4. Conclusion

The CaF$_2$ nanostructures were synthesized from Ca-silicide powders by an HF treatment. It was found that the morphology of the resulting products depends on the starting materials. The morphological control of the CaF$_2$ nanostructure was demonstrated by the HF treatment of the appropriate Ca-silicide as the starting material. As the starting material, when CA-CaSi$_2$ crystals were used, polycrystalline CaF$_2$ nanosheet bundles were formed. On the other hand, when MA-calcium silicide was used, CaF$_2$ nanobunches or nanoparticles were formed. The results suggest that further control of the morphological and structural properties of the CaF$_2$ nanostructures would be possible by a simple chemical reaction in an HF solution using calcium silicides as the source materials, which would allow us to apply the nanostructures to many applications in various fields.

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Fig. 6. SEM image and corresponding EDS mappings of the powder consisting of the CaF$_2$ nanobunches of nanoparticles synthesized from the MA-calcium silicide powders by the HF treatment.
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