Surfactant-Free Synthesis of CaSO₄ Nanorod/Nanowire by Electrochemical Deposition

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High density and ordered CaSO₄ nanorods and nanowires were prepared on a Au-coated Si substrate by electrochemical deposition in a dimethylformamide solution of calcium chloride and thionyl chloride. This approach represents a synthetic route for a rapid and large-scale preparation of CaSO₄ one-dimensional nanostructures. The lengths and diameters of the nanorods and nanowires were controlled by regulating the concentration of the precursor solution. It is suggested that the morphology of the CaSO₄ nanorods and nanowires strongly depends on both the chloride ion and water concentration. The formation mechanism of CaSO₄ on the substrate and in solution is believed to be the result of electrochemical reactions increasing the concentration of sulfate ions via a reaction with calcium cations. During the growth process of CaSO₄, the chloride ion was adsorbed to a specific side of the CaSO₄ nanostructures such that nanorods and nanowires were grown in one direction.

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Manuscript submitted June 10, 2009; revised manuscript received November 10, 2009. Published January 4, 2010.

In recent years, significant interest has focused on the synthesis of nanoscale materials. One-dimensional (1D) nanostructures such as nanowires, nanotubes, and nanorods have become the focus of intensive research due to their unique properties and potential applications in energy, optic, electric, and sensor systems. Furthermore, 1D nanostructures have been shown to provide a framework for applying the bottom-up method for designing the nanostructures. Many methods exist for the synthesis of 1D nanostructures, including chemical vapor deposition, a template-assisted method, and a vapor–liquid–solid method. In particular, both electrochemical deposition and liquid phase methods synthesize 1D nanostructures in liquid and have been used by many research groups because there is no need to use high temperature, expensive instruments or templates. Despite the advantages of synthetic simplicity, there are some challenges in the application process. For the synthesis of 1D nanostructures, electrochemical deposition and liquid phase synthesis methods need surface-active agents or amphiphilic polymers as stabilizing or capping agents to control the shape, length, and diameter. For various application fields, surfactant or amphiphilic polymers should be removed by multiple rinsing. However, some surfactants or amphiphilic polymers may still be bound to the 1D nanostructure surface. Thus, surfactant-free and amphiphilic polymer-free systems have been suggested.

Calcium sulfate is one of the most attractive inorganic materials for applications in bone regeneration and drug delivery because of its resorbable scaffold for bone growth to supply calcium ions, biocompatibility, possibility as a drug delivery vehicle, and low cost. In addition, rare-earth-doped CaSO₄ shows useful thermoluminescence for the potential application in photoluminescence crystal liquid displays, optical storage materials, and cathodoluminescent materials.

Various methods have been used for the synthesis of CaSO₄ nanoparticles, nanorods, nanowires, and nanosheets, such as water-in-oil microemulsion and reverse micelles, a microwave-assisted method, and a liquid–liquid separation method. However, these methods have limitations in growth time, large quantity synthesis, and substrate synthesis. Alternatively, the electrochemical deposition method is a promising synthetic technique because of low cost, mild conditions, accurate process control, fast reaction time, and large quantity synthesis.

In this study, CaSO₄ nanorods and nanowires were synthesized by electrochemical deposition in an electrolyte solution without surfactants. We examined the effects of CaCl₂, SOCl₂, and water concentration on the formation of CaSO₄ nanorods and nanowires. A possible mechanism of the growth of CaSO₄ nanorods and nanowires on a Au-coated Si substrate in solution was identified.

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CaCl₂ was greater than 0.005 M. When the concentration of CaCl₂ was 0.001 M, CaSO₄ nanosheets were observed on the substrate. Further additions of chloride anions caused the formation of CaSO₄ nanorods (Fig. 2b and c) and eventually increased the length of the CaSO₄ nanorods (Fig. 2d). The chloride anion concentration is very important for determining the shape and length of a nanostructure, and high concentrations of chloride anions typically increase the average length of nanorods. Based on this result, the chloride anion can act as a capping reagent to change the growth kinetics and surface energies of different crystal faces, which can lead to anisotropic growth of CaSO₄ nanorods.

Water effects.—Figure 4 shows typical CaSO₄ nanowires grown on the substrate with 0.5 mL of DI water added to the 10 mL of electrolyte. It means that there was 2.5 M water in the cells. In a previous experiment where no water was added, only 0.1 M water was expected to exist in the cell from the calculation based on the purity of DMF (99.8%). DI water reacted with SOCl₂ to produce SO₄²⁻, thereby increasing the amount of sulfate anions in the electrolyte solution. The increase in SO₄²⁻ meant that the calcium cations more easily reacted with SO₄²⁻ to synthesize CaSO₄ nanostructures, and the growth rate and yield of CaSO₄ increased, resulting in nanowires instead of nanorods. Figure 4a and b is an SEM image of CaSO₄ synthesized in 0.01 M CaCl₂, 0.1 M SOCl₂, and DI water. CaSO₄ nanowires were straight with diameters of 50–200 nm and lengths of 17.71 nm with 0.01 M CaCl₂ and 0.05 M SOCl₂ (Fig. 3b). Additionally, 0.01 M CaCl₂ and 0.1 M SOCl₂ (Fig. 3c) had 2252 ± 225.77 and 89 ± 15.43 nm, respectively. These histograms clearly demonstrate that the concentrations of CaCl₂ and SOCl₂ affect the lengths, diameters, and shapes of CaSO₄ nanorods.

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lengths of up to tens of micrometers. Figure 4c and d shows the ordered CaSO₄ nanowires arrayed in nanobelt-like structures synthesized in 0.05 M CaCl₂, 0.1 M SOCl₂, and DI water. As shown in Fig. 4c, vertically aligned CaSO₄ nanowires were attached at their ends and distributed uniformly on the surface. The structural differences between the 0.01 and 0.05 M CaCl₂ conditions appear to be due to the different calcium cation concentrations. Several studies have demonstrated the structural differences between nanowires and nanobelts caused by growth and nucleation rates.31,32 CaSO₄ nanowires were preferably formed under slow nucleation and slow growth rates, whereas the CaSO₄ nanowires arrayed into nanobelt-like structures formed under fast nucleation and growth rates.

When CaSO₄ nanowires were synthesized on the substrate, CaSO₄ nanorods were simultaneously synthesized in solution. In the synthetic process, the color of the electrolyte rapidly changed to white. To observe the CaSO₄ nanorods in solution, the opaque electrolyte solution was spin-coated directly onto the Si substrate at 3000 rpm. Figure 5 shows the CaSO₄ nanorods synthesized in 0.1 M SOCl₂ + 0.05 M CaCl₂ and DI water conditions. When water was added to the electrolyte, the CaSO₄ nanowires and nanorods were simultaneously synthesized on the substrate and in solution, respectively. When voltage was applied to the electrodes, the substrate was covered by CaSO₄ nanowires and the solution changed from colorless and transparent to white and turbid. When the reaction was complete, the substrate surface was fully covered with CaSO₄ nanowires. However, when water was not added to the electrolyte, the CaSO₄ nanorods were only synthesized on the substrate. This result showed that when the concentration of sulfate anions was low, the CaSO₄ nanorods were first synthesized on the substrate. However, CaSO₄ was not synthesized in the solution because most of the sulfate anions reacted with calcium cations on the substrate surface. However, if the concentration of sulfate anions is high, the CaSO₄ nanorods may synthesize on the substrate surface and in solution simultaneously.

**Conclusions**

In summary, we have successfully synthesized CaSO₄ nanorods and nanowires both on a substrate and in a DMF solution using an electrochemical deposition method. The concentration of CaCl₂, SOCl₂, and water influenced the formation and morphology of CaSO₄ nanorods and nanowires. CaCl₂ and SOCl₂ supply chloride anions for controlling the morphology of CaSO₄ nanostructures, and water provides sulfate anions by an electrochemical reaction with SOCl₂. A high concentration of SOCl₂ and CaCl₂ permits the synthesis of nanorods and nanowires on a substrate and in solution. It is expected that this synthetic method may also be applicable for the fabrication of other inorganic nanorods and nanowires.

**Acknowledgments**

Financial support for this research was provided by the Korea Foundation for International Cooperation of Science and Technol-
ogy (KICOS) and the National Program for Tera-Level Nanodevices by the Ministry of Education, Science and Technology of Korea.

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