Inorg. Chem. **2007**, *46*, 7707–7709

Inorganic Chemistry
Communication

In Situ Hydrothermal Synthesis of Nanolamellate $CaTiO_3$ with Controllable Structures and Wettability

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Received April 24, 2007

Nanolamellate structures of $CaTiO_3$ were fabricated by using an in situ hydrothermal synthesis method on titanium for the first time. The number of nanolamellas and the morphology completely or mainly depend on the reaction time and NaOH concentrations, and the wettability of the resulting $CaTiO_3$ surfaces can be successively turned from superhydrophilic to superhydrophobic after modification with a thin layer of hydrophobic silicone, mainly depending on the surface morphology. The proposed formation mechanism of the nanolamellate $CaTiO_3$ structures has also been discussed.

Over the past few years, the investigation into nanostructured materials (1-D, 2-D, and 3-D) has become one of the most concentrated research areas.[1−3] The synthesis of hierarchical nanostructure materials with controllable sizes, shapes, and dimensions, which possess substantially enhanced properties compared with bulk materials, has become a dream of chemists and materials scientists. Complex oxides with a perovskite structure began to attract wide attention because of their potential applications in a number of areas such as ferroelectricity, ferromagnetism, colossal magnetoresistance, semiconductors, luminance, and optoelectronics.[4−8] Calcium titanium ($CaTiO_3$) as a perovskite material is a promising material for communication equipment operating at microwave frequencies because of the high dielectric constant, high dielectric loss, and large positive temperature coefficient of the resonant frequency.[9] In addition, $CaTiO_3$ formed on titanium implants could increase osteoblast adhesion on hydroxylapatite and so greatly improves implant efficacy.[10]

Up until now, $CaTiO_3$ was usually synthesized by a solid-state reaction between TiO_2 and $CaCO_3$ or CaO at a high temperature or prepared by mechanochemical methods. Recently, Pontes and his co-workers[11] prepared $CaTiO_3$ powders by the polymeric precursor method, and Manik and Pradhan[12] fabricated $CaTiO_3$ by high-energy ball milling of the equimolar mixture of CaO and anatase (a)−TiO_2 powders. However, these methods all produce $CaTiO_3$ with special topographies with difficulty. Despite the extensive work reported, we are not aware of studies that fabricated a nanolamellate structure of $CaTiO_3$. Herein, we report a simple approach to synthesize 3-D lamellate $CaTiO_3$ structures via an in situ hydrothermal method on the titanium substrate for the first time. The wettability of the $CaTiO_3$ surfaces can be successively tailored from superhydrophilic to superhydrophobic after modification with a thin layer of hydrophobic silicone [poly(dimethylsiloxane) vinyl-terminated (PDMSVT)]. These resulting materials can be very useful in sensors, antifogging materials, medicine, and biomaterials.

Parts a and b of Figure 1 show typical scanning electron microscopy (SEM) images of the as-prepared $CaTiO_3$ at low and high magnification, respectively. It is clearly seen that a large number of beautiful $CaTiO_3$ structures were uniformly formed, covering the substrate back-to-back, and the shapes of these structures were similar to those of roses. More detailed information of the surface structure, included in the high-magnification SEM image shown in Figure 1b, indicated that the petals, connected with each other closely, with a

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10.1021/ic700777f CCC: $37.00 © 2007 American Chemical Society
Published on Web 08/14/2007

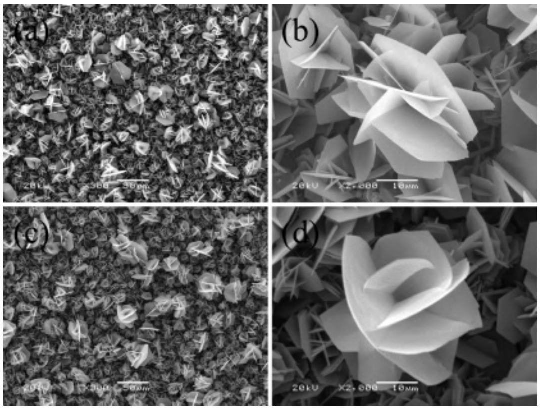

Figure 1. SEM images of the $CaTiO_3$ nanolamellate structures on the titanium substrate before and after heat treatment. Low- (a) and high-magnification (b) images of the surface structures before heat treatment and low- (c) and high-magnification (d) images of the same sample after heat treatment at 400 °C for 2 h.

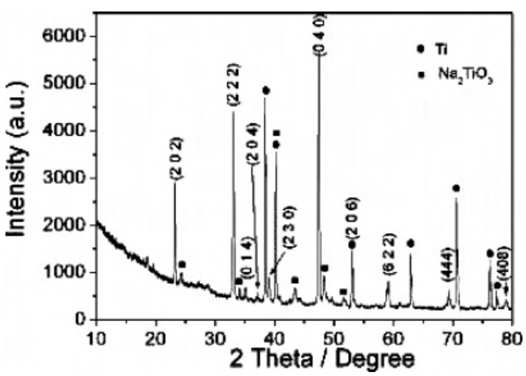

Figure 2. XRD pattern of the as-prepared surface on the titanium substrate.

width of about 10 μm, formed the 3-D lamellate $CaTiO_3$ structure. It is also clearly seen that the petal is about 100−200 nm in thickness from the field emission SEM (FESEM) images shown in the Supporting Information Figure S3. To investigate the thermal stability of the as-prepared $CaTiO_3$ on the substrate, we also studied the SEM image of the as-prepared surface after being annealed at 400 °C for about 2 h, as shown in parts c and d of Figure 1, respectively. It is clear that the morphology is similar to that of the origin sample prior to treatment, suggesting that the as-prepared surface of $CaTiO_3$ has good thermal stability. It is also noted that the as-prepared $CaTiO_3$ did not fall from the titanium substrate, showing that the adhesion between the $CaTiO_3$ nanolamellate structures and the substrate is very well, which is very important for the potential applications of the as-prepared surfaces in various fields.

The corresponding X-ray diffraction (XRD) pattern recorded from the as-prepared surface is shown in Figure 2. Ten sharp diffraction peaks marked with Miller exponents can be indexed to $CaTiO_3$ [Joint Committee on Powder Diffraction Standards (JCPDS) card no. 09-0365]. All of the peaks marked by ● come from the titanium substrate. The peaks marked by ■ are characteristic of Na_2TiO_3 (JCPDS no. 37-0345), which is also formed on the surface. Energy-dispersive X-ray analysis (EDS) was also performed on different areas so as to further verify the composition of the flowerlike structures and underneath substrates (see Figure S8 in the Supporting Information). A strong signal of the element calcium was detected in the lamellate structure area and only a very weak signal of calcium in the porous titanium substrate microstructure area, further indicating that the lamellate structure is indeed $CaTiO_3$.

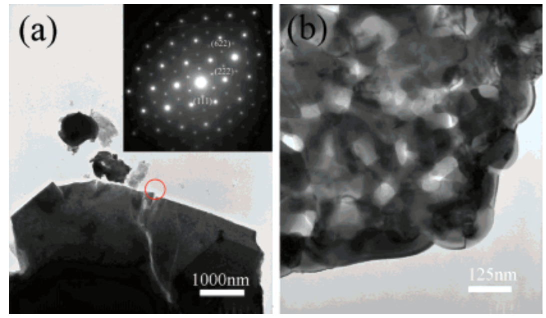

Figure 3. (a) TEM image of one petal of the $CaTiO_3$ nanolamellate structures. The inset shows the corresponding SAED pattern. (b) High-magnification TEM image of the sample shown in part a marked by a circle.

Figure 3a shows transmission electron microscopy (TEM) images of the petals scratched from the prepared lamellate $CaTiO_3$ structures. Figure 3b is the amplificatory image of the sample shown in Figure 3a marked by a red circle. Also, the corresponding selected area electron diffraction (SAED) pattern shown in the upper right inset of Figure 3a displays the typical spot pattern of a well single-crystal structure of the sample.

The present method is based on isotropic etching of titanium by a base solution at high temperature and instant growth of $CaTiO_3$ in the presence of $Ca(OH)_2$. The size, shape, and dimensionality of the as-prepared lamellate $CaTiO_3$ are apparently impacted by the solution concentration, reaction time, temperature, etc. The reaction temperature directly determined the formation of $CaTiO_3$ structures. It is found that few $CaTiO_3$ lamellate structures were generated below 100 °C or above 150 °C. Also, the effect of the NaOH concentration and reaction time on the morphologies of the as-prepared $CaTiO_3$ structures is discussed in the Supporting Information. The size and shape of the flowers can be controlled by adjusting the reaction time and concentrations of the reactants.

The growth of lamellate $CaTiO_3$ in the hydrothermal condition is achieved for the first time. Although the exact growth mechanism is not very clear, we believe that NaOH plays a very important role. The titanium substrate first reacts with a NaOH solution to form Na_2TiO_3, and then the resultant Na_2TiO_3 reacted with the $Ca(OH)_2$ supersaturation solution to obtain an insoluble solid $CaTiO_3$. To simplify the expression for chemical reactions, we can see that[13,14]

$$Ti + 2NaOH + H_2O \rightarrow Na_2TiO_3 + 2H_2 \qquad (1)$$

$$Na_2TiO_3 + Ca(OH)_2 \rightarrow CaTiO_3 + 2NaOH \qquad (2)$$

Investigations of the concentration- and time-dependent shape-evolution processes (see Figures S2 and S3 in the Supporting Information) indicated that first the $CaTiO_3$

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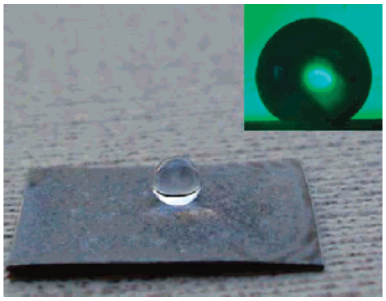

Figure 4. Shape of a water droplet (about 10 mg) on the surface only covered by the nanolamellate structures after PDMSVT modification, with a water contact angle of about 160 ± 1.6°.

particles are formed as seed and then they generate a suitable amount of $CaTiO_3$ cluster nuclei for subsequent growth, and each nanocluster has its own orientation. During the hydrothermal process, Na_2TiO_3 and $Ca(OH)_2$ react continuously and form a large number of $CaTiO_3$ nanoparticles. The nanoparticles aggregate on the nanocluster and grow up to nanolamellate petals to assemble the $CaTiO_3$ lamellate structure. With a prolonging of the reaction time, the size of the lamellate structures increases, and the structures change their complexity accordingly (Figure S9 in the Supporting Information). In the same way, titanium reacts with high-concentration NaOH to form more quickly and form more $CaTiO_3$ particles to assemble the lamellate structure. So, the high-concentration NaOH would accelerate the formation of the $CaTiO_3$ lamellate structures to a certain extent.

We further investigated the wetting properties of the $CaTiO_3$ lamellate structures. Wettability, a very important aspect of materials, is governed by both the surface chemical composition and the geometric structure.[15,16] The wettability of the as-prepared surface on the titanium substrate could be turned from superhydrophilicity to superhydrophobicity by applying a spinning coating process with PDMSVT. Figure 4 presents the wetting properties of water droplets on the $CaTiO_3$ sample after modification by PDMSVT similar to our previous work.[17,18] As we known, a drop of water spreads extensively on the $CaTiO_3$ surface with a contact angle of less than 10°,[19,20] indicating that the surface of the $CaTiO_3$ lamellate structure is superhydrophilic (Figure S7 in the Supporting Information). The reason is due to the capillary effect. It is very interesting that the same sample modified by PDMSVT shows superhydrophobicity with a water contact angle of about 160°. It is currently unclear why the as-prepared surface modified with PDMSVT shows superhydrophobic, compared to the surface of the $CaTiO_3$ lamellate structure and the pure titanium plate with the same treatment (Figures S5 and S6 in the Supporting Information), regardless of the surface free energy. However, it is very important for this functional surface applied in various industrial fields, such as antifogging, self-cleansing, drag reduction, and anticorrosion.

In summary, new controllable nanolamellate $CaTiO_3$ structures were successfully fabricated through an in situ hydrothermal method on the titanium surface. This method may be applied to synthesize other materials of special structures, including $BaTiO_3$, $MgTiO_3$, $SrTiO_3$, $ZnTiO_3$, and other systems.

Acknowledgment. The authors gratefully acknowledge the NSFC (Grant 50421502) and the National 973 Project (Grant 2007CB607601) and thank Dr. Feng Zhou for fruitful discussions.

Supporting Information Available: Preparation and characterization of the nanolamellate $CaTiO_3$ materials, FESEM and TEM photographs, EDS results, the effect of the NaOH concentration and reaction time on the morphologies of $CaTiO_3$ structures, and the contact angle images. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700777F

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