Reverse Micelle Based Formation of BaCO$_3$ Nanowires

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A reverse micelle based approach is reported for the synthesis of BaCO$_3$ nanowires with lengths up to 100 μm and diameters as small as 10−30 nm, each of which is a continuous single crystal with the *c*-axis along the wire length axis. The synthesis is achieved by the reaction of barium and carbonate ions solubilized in the polar cores of nonionic reverse micelles of C$_{12}$E$_4$ (tetraethylene glycol monododecyl ether) in cyclohexane. The crystal growth of BaCO$_3$ nanowires has been examined by electron microscopy observations, and a directional aggregation process is proposed for the nanowire formation.

Introduction

Recently, the preparation and properties of nanowires of various materials have received considerable attention, and the potential wide-ranging applications of this kind of nanomaterials have been predicted.[1−6] For the fabrication of nanowires of desired materials, the template method has been demonstrated to be very effective; examples include the use of carbon nanotubes[1−3] and the nanochannels in nuclear track polycarbonate membranes[4] or porous alumina[5,6] as hard templates within which desired materials are synthesized. In addition, certain "soft template" methods[7] may be applied although soft templates cannot always regulate the size and shape of the products; for instance, rodlike cationic surfactant micelles have been used as templates for the preparation of rodlike gold particles.[8] It will be interesting to explore the possibility of solution-based synthesis of nanowires without the presence of preformed templates.

As organized media, reverse micelles or microemulsions have been widely used as spatially constrained microreactors for controlled synthesis of inorganic nanoparticles.[9−11] In most cases, spherical nanoparticles are formed within the polar cores of reverse micelles under certain conditions; the reported examples include cylindrical copper particles,[12] cubic BaSO$_4$ particles,[13] and rodlike and ellipsoidal BaCO$_3$ particles.[14] Recently, reverse micelles or microemulsions have also been used for controlled growth of macroporous and microporous crystals. For instance, bicontinuous reverse microemulsions have been used as preorganized systems for the fabrication of crystalline calcium phosphate materials with extended reticulated microstructures.[15] On the other hand, microporous zincophosphate sodalite with a cubic morphology has been synthesized in reverse micelles, indicating that the reverse micelle based approach can provide a means of controlling the morphology as well as the size of growing crystals.[16,17]

These studies motivated us to explore if reverse micelles can be used to form nanowires of inorganic materials. The results obtained from preparation of BaCO$_3$ nanoparticles in reverse micelles by the CO$_2$ bubbling method have shown that while only spherical particles are formed in ionic reverse micelles,[18] rodlike and ellipsoidal particles can be obtained in nonionic reverse micelles.[14] The obtained rodlike BaCO$_3$ particles have axis ratios as large as 23−39, which may be the largest axis ratio for the asymmetrical nanoparticles synthesized in reverse micelles to date. Thus, it is preferable to choose BaCO$_3$ as the material to form nanowires with large axis ratio in reverse micelles.

In this paper, we report the synthesis of BaCO$_3$ nanowires with lengths up to 100 μm and diameters as small 10−30 nm, each of which is a continuous single crystal with the *c*-axis along the wire length axis, by the reaction of barium and carbonate ions solubilized in the polar cores of nonionc reverse micelles. The results from electron microscopy observations of crystal growth indicate that the BaCO$_3$ nanowires are formed in reverse micelles by the directional aggregation process.

Experimental Section

The nonionic surfactant C$_{12}$E$_4$ (tetraethylene glycol monododecyl ether) was obtained from Acros Organics, Belgium, and was used without further purification. Cyclohexane, BaCl$_2$·2H$_2$O, Na$_2$CO$_3$, CaCl$_2$, and Na$_2$SO$_4$ were of A.R. grade, and the water used in this work was deionized and distilled.

A nonionic reverse micelle system, C$_{12}$E$_4$/cyclohexane/water, was selected for this study, which has been characterized previously.[19,20] A typical procedure for formation of BaCO$_3$ nanowires with large axis ratio in C$_{12}$E$_4$ reverse micelles is outlined below. The reverse micelles were prepared by solubilizing an aqueous solution containing Ba^{2+} or CO$_3^{2-}$ ions into a 0.2 M solution of C$_{12}$E$_4$ in cyclohexane to give a water content of 2 vol %. The reactant ion concentration in the aqueous solution was 0.1 M. The synthesis of BaCO$_3$ nanowires was achieved by mixing rapidly the same volume of two reverse micelle solutions with barium ions (BaCl$_2$) in one solution and carbonate ions (Na$_2$CO$_3$) in the other at ambient temperature (18 °C). The resulting suspension remained stable (no evidence of settling was observed) for several days. For comparison, BaSO$_4$ and CaCO$_3$ particles were also synthesized in an identical manner, using Na$_2$SO$_4$ instead of Na$_2$CO$_3$ and using CaCl$_2$ instead of BaCl$_2$, respectively.

A JEM-200CX transmission electron microscope (TEM) was used to characterize the morphology and structure of the products at an accelerating voltage of 200 kV. Samples for TEM analysis were prepared at different intervals of aging time by dropping a drop of the reverse micelle solutions containing the products onto a Formvar-covered copper grid placed on filter paper and drying in air at room temperature. Prior to the extraction of samples, the reverse micelle solutions were gently shaked several times.

Results and Discussion

After an aging time of 2 days, BaCO$_3$ nanowires synthesized in C$_{12}$E$_4$ reverse micelles are long wires in shape, with lengths up to 100 μm and diameters ranging from 10 to 30 nm. Three

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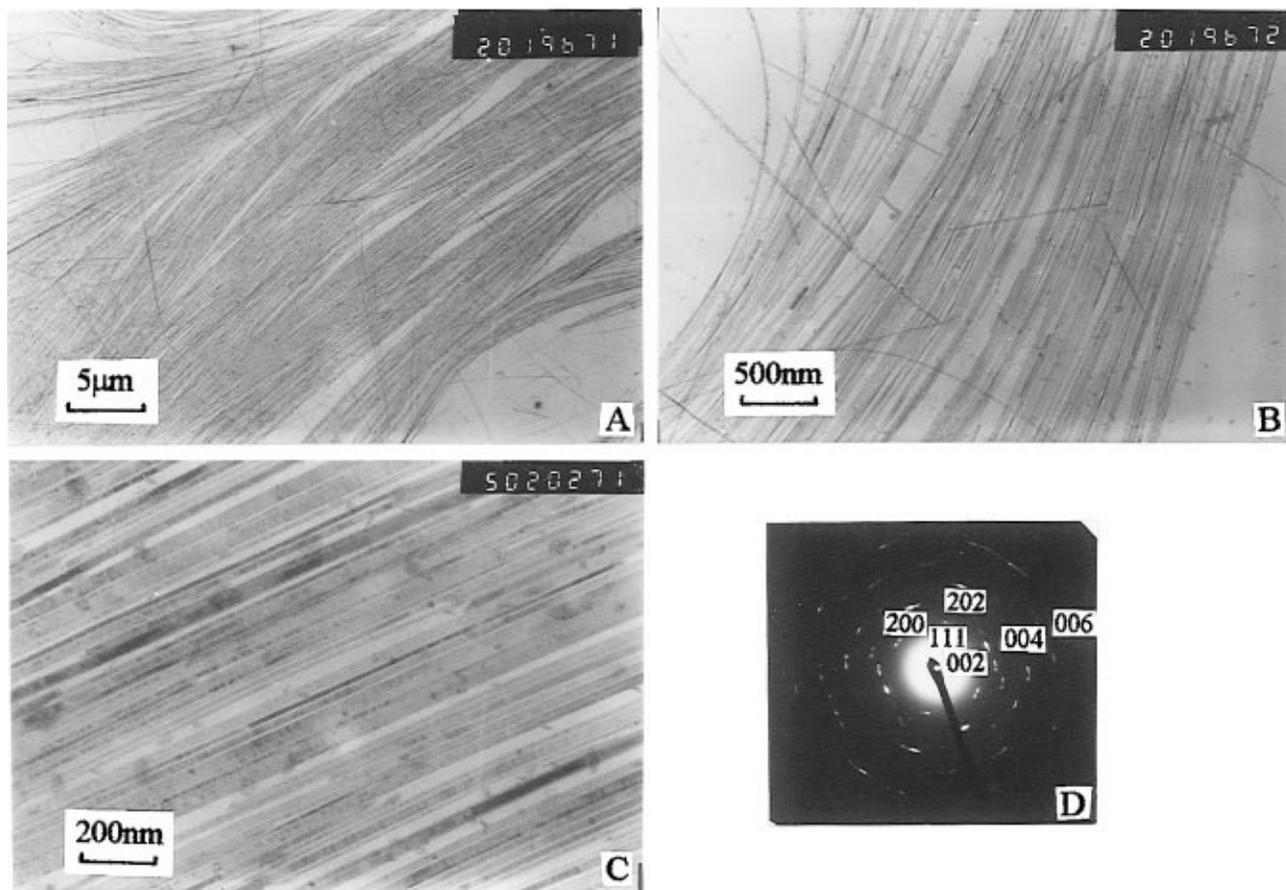
Figure 1. TEM micrographs and electron diffraction pattern of $BaCO_3$ nanowires synthesized in $C_{12}E_4$ reverse micelles and aged for 2 days. (A−C) TEM micrographs with different magnifications. (D) Electron diffraction pattern from the whole area shown in (C).

TEM micrographs with different magnifications, along with a representative electron diffraction pattern, are given in Figure 1. As shown in Figure 1A, the long wires are apparently continuous and form a rather regular two-dimensional nanowire array in a large area. It can be seen from the micrograph with a higher magnification (Figure 1B) that although some shorter or broken wires are indeed present, a large number of wires are continuous. Figure 1C, which has an even higher magnification, clearly shows that the wires with most diameters in the range of 10−30 nm are regularly arrayed and approximately parallel to each other. The corresponding electron diffraction pattern (Figure 1D) reveals a typical diffraction pattern due to a preferentially oriented fibrous texture. The diffraction pattern identifies that the $BaCO_3$ nanowires are crystals of orthorhombic witherite structure with lattice constants of $a = 5.31$ Å, $b = 8.90$ Å, and $c = 6.43$ Å. Moreover, it is also shown that only (00L) spots can be observed along the fiber axis, indicating that each wire is a single crystal with the c-axis along the wire length axis. Further study on electron diffraction patterns from single wires reveals that all the patterns display diffraction spots instead of rings and the observed (00L) spots are always along the wire length axis. This result confirms that the $BaCO_3$ nanowires are single crystals with a preferential growth direction along the c-axis.

The obtained $BaCO_3$ nanowires can reach 100 μm in length, resulting in aspect ratios as large as 10 000 (length $\sim$ 100 μm and diameter $\sim$ 10 nm), which is much larger than those of the nanowires obtained previously from templates of nanotubes[3] or porous alumina.[6] It is extremely unusual to obtain such long wires from reverse micelle solutions, in which no preformed templates could be demonstrated to be present. The time-resolved fluorescence quenching and dynamic light scattering

studies on the ternary reverse micelle system $C_{12}E_4$/cyclohexane/water have shown that the reverse micelles in this system can be regarded as spherical and their sizes are usually less than 10 nm.[20] Although the presence of the reactant ions may induce the change in the micellar size and shape, it is not likely to lead to the formation of water nanochannels in oil, such as those formed in bicontinuous reverse microemulsions,[15] at such a low water content (2 vol %). Since the template mechanism of the nanowire formation in reverse micelles could be excluded, it is worthwhile to examine the crystal growth of the nanowires in reverse micelles.

Figure 2 presents the TEM micrographs at early stages of the nanowire formation. As shown in Figure 2A, the sample obtained in $C_{12}E_4$ reverse micelles and aged for 5 min exhibits many tiny particles which have been revealed to be amorphous by the corresponding electron diffraction. It is noteworthy that there is evidence of some very thin wires as indicated by the arrows, which may be the crystal nuclei to grow into the final crystalline nanowires. After an aging time of 30 min, many particles are aggregated along the preformed thin wires (Figure 2B); however, the electron diffraction does not show the presence of crystals. When aged for 5 h, the aggregates along the wires become much denser, and the electron diffraction pattern clearly exhibits diffraction rings and spots due to witherite structure $BaCO_3$ crystals, indicating the presence of $BaCO_3$ polycrystals together with individual monocrystal (Figure 2C). A micrograph with a lower magnification is given in Figure 2D, which shows that those polycrystals-based nanowires have lengths up to several micrometers. The micrograph of the sample obtained after an aging time of 1 day, as shown in Figure 2E, suggests that the polycrystals-based nanowires have been reconstructed into monocrystals-based wires ranging from
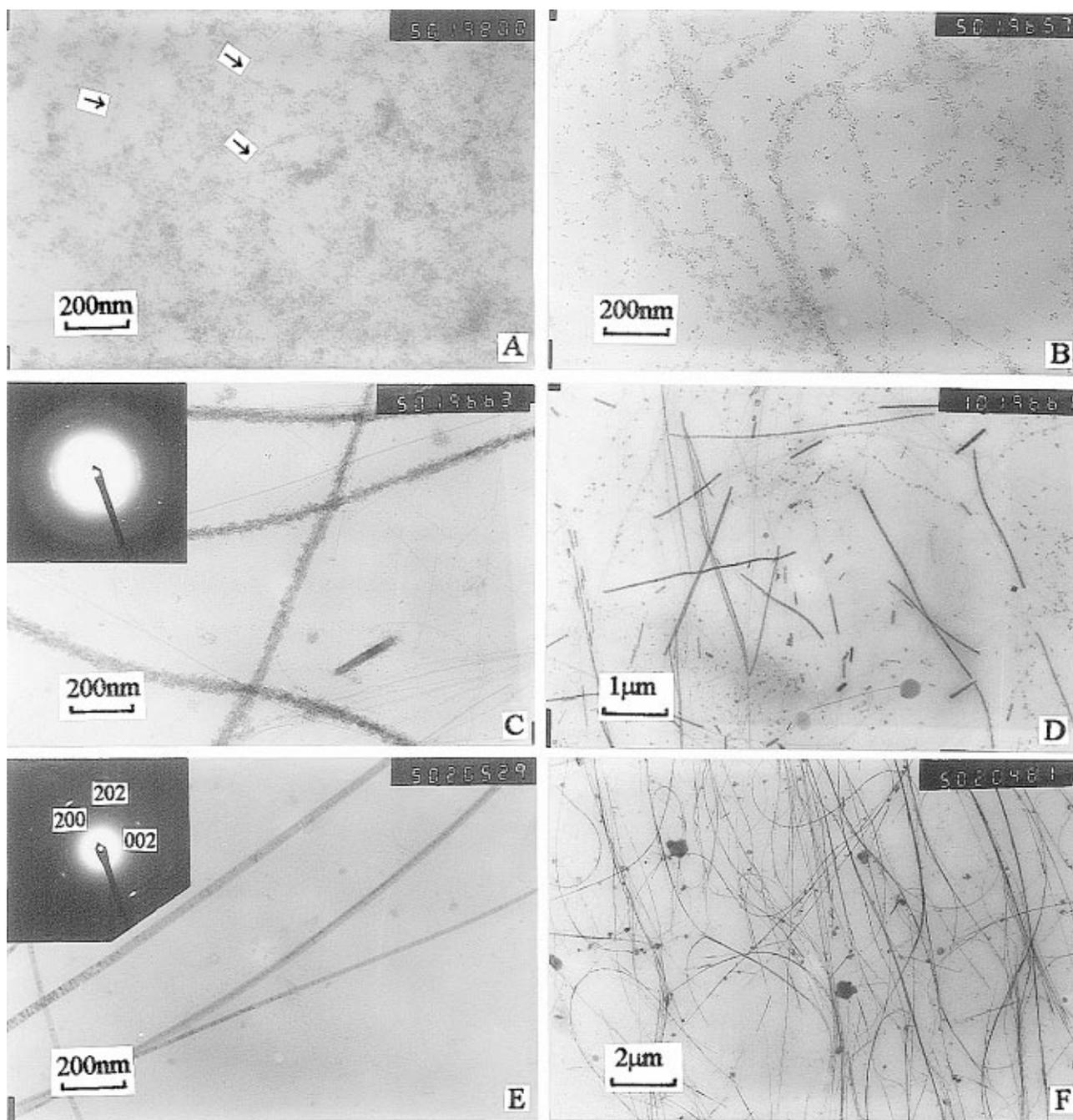
Figure 2. TEM micrographs and electron diffraction patterns of $BaCO_3$ samples obtained in $C_{12}E_4$ reverse micelles and aged for: (A) 5 min, (B) 30 min, (C, D) 5 h, and (E, F) 1 day. Inset in (C) shows the electron diffraction pattern from the whole area shown in (C) and inset in (E) shows that from the top single wire in (E).

10 to 30 nm in diameter, which have the *c*-axis along the wire length axis as indicated by a representative electron diffraction pattern of a single wire. A micrograph with a lower magnification shown in Figure 2F reveals that the formed nanowires have grown to several tens of micrometers in length. After one more day of aging, these wires develop into the nanowires shown in Figure 1, which are even longer in length but almost the same in diameter. The interaction between such long wires, along with the possible adsorption of the surfactant on the wires, may contribute to the formation of the rather regular nanowire array when the nanowires are transferred to solid supports by evaporation of the solvent.

These TEM observations of the crystal growth of the $BaCO_3$ nanowires in reverse micelles suggest that the nanowires could be formed by a directional aggregation process which has been established for the formation of some monodisperse inorganic colloidal systems.[21] For example, study on the formation of α-Fe_2O_3 ellipsoidal particles in the presence of KH_2PO_4 has indicated that after hematite nucleation, phosphate groups adsorb on surface planes parallel to the *c*-axes of the nuclei, resulting in the growth of anisometric primary particles, which then aggregate in a directional manner through their *c*-axes, with phosphate desorption, producing the final ellipsoidal mono-crystal particles with the *c*-axis along the length axis.[22] In the present case, it is tentative to assume that after $BaCO_3$ nucleation in $C_{12}E_4$ reverse micelles, the surfactant headgroups preferentially adsorb on surface planes parallel to the *c*-axes of the primary nuclei, resulting in the formation of the thin-wire-like nuclei with the *c*-axis along the wire length axis, which may be too small to exhibit crystallinity to the electron diffraction. Then, the amorphous tiny particles, which could be also developed from the primary nuclei, aggregate onto the thin wire

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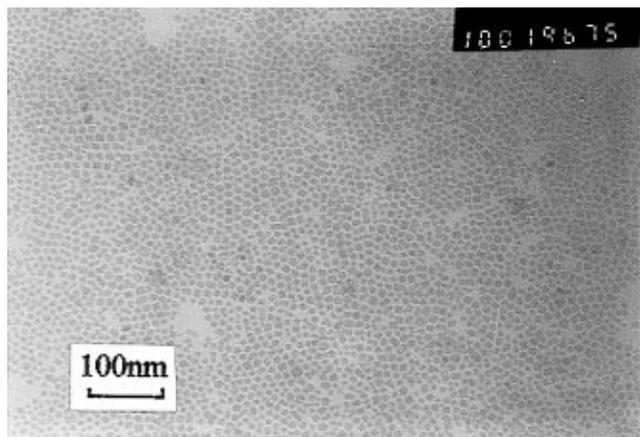
Figure 3. TEM micrograph of BaSO$_4$ nanoparticles synthesized in C$_{12}$E$_4$ reverse micelles and aged for 1 day.

in a directional manner, with surfactant desorption and BaCO$_3$ crystallization, producing the nanowires of single crystals. On aging, pairs of wires may be coupled through their *c*-axes, leading to the increase in the wire length. Although such a proposed mechanism remains to be confirmed by more detailed investigation, it is evidenced that the BaCO$_3$ nanowires of single crystals are formed by an aggregation growth rather than the layer-by-layer growth proposed for the zincophosphate sodalite with a cubic morphology in AOT reverse micelles.[17] It seems that the C$_{12}$E$_4$ reverse micelles provide significant control over the directional nucleation and aggregation growth of the BaCO$_3$ nanowires. It is noteworthy that our preliminary investigation has shown that composition conditions of reverse micelles, such as water content, C$_{12}$E$_4$ concentration, and reactant ion concentration, can significantly affect the lengths of the BaCO$_3$ nanowires but have relatively little effect on the nanowire diameters. However, the reason why the nanowire diameters are limited to certain size range is not yet known.

For comparison, we have carried out analogous experiments with BaSO$_4$ and CaCO$_3$ which are simple inorganic materials like BaCO$_3$. However, only nanoparticles with symmetrical shapes can be obtained in both cases. It is found that while the obtained CaCO$_3$ nanoparticles are spherical, BaSO$_4$ nanoparticles formed in C$_{12}$E$_4$ reverse micelles are approximately cubic (Figure 3), which is similar to the situation of BaSO$_4$ nanoparticles prepared in nonionic Triton X-100 reverse micelles.[13] These results indicate that in addition to the morphology control provided by the reverse micellar environment, the crystal habits of inorganic materials play an important role in the formation of the final morphology of the materials. With regard to the formation of BaCO$_3$ nanowires, the nanowire formation is probably facilitated by the acicular habit of BaCO$_3$ crystals. The reported results from the construction of reticulated framework in reverse bicontinuous microemulsions have also shown that such construction is facilitated by the needle-like morphology of the hydroxyapatite crystals.[15] Since the final morphology of inorganic crystals formed in reverse micelles reflects a compromise between the constraints of crystal physics and the morphology control provided by reverse micelles, synthesis of inorganic nanowires of other materials in reverse micelles might be achieved by selecting suitable reverse micelle systems.

Our results demonstrate that reverse micelles can be used for the solution-based synthesis of inorganic nanowires of single crystals with a preferential growth direction. Such a reverse micelle based approach provides a new chemical route to inorganic nanowires, which may find applications in many technological fields.

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