Synthesis of $BaCO_3$ Nanowires and Nanorods in the Presence of Different Nonionic W/O Microemulsions

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Several one-dimensional nanomaterials(wires and rods) of $BaCO_3$ were synthesized in the presence of the nonionic w/o micro-emulsions of Tween-80, Triton X-100 and $C_{12}E_9$. The intermediate and middle course of $BaCO_3$ nanowires formation were captured, and the formation mechanism of the one-dimensional nanomaterials was conjectured as directional aggregation of $BaCO_3$ colloid particles controlled by soft microemulsion template.

In recent years the interest in fabrication and properties of one-dimensional nanostructured materials has constantly grown because of their potential wide-ranging applications in optics, electricity, nano-electronics, and others.[1-4] Although a few methods (for example, the hard template control growth method,[5-8] the high temperature gas phase growth method[9,10] and so on) have been used for the preparation of one-dimensional nanostructured materials, the procedures are complex and the conditions are harsh. Recently, microemulsions or reverse micelles have been widely used as spatially constrained microreactors for controlled synthesis of inorganic nanoparticles.[11,12] So, it is possible to explore the fabrication of some new one-dimensional nanostructured materials through microemulsions or reverse micelles methods. In this paper, a new synthesis result of a few kinds of $BaCO_3$ products with the preferential growth (nanowires, nanorods, etc.) in the presence of nonionic w/o microemulsions is reported, and the formation mechanism is explored. It will open a new synthetic route for a series of one-dimensional nanostructured materials.

In this study, the microemulsion systems of three kinds of nonionic surfactants–Tween-80 [polyoxyethylene(20) sorbitan oleic ester], Triton X-100 [polyoxyethylene(9) 4-(1,1,3,3-tetramethylbutyl)phenyl ether] and $C_{12}E_9$ [polyoxyethylene(9) dodecyl ether] were used for preparation of one-dimensional nanostructured $BaCO_3$. The optimal synthetic conditions and the morphology and structure of the products for the three systems were investigated.

One-dimensional nanostructured $BaCO_3$ was prepared according to the following procedure. Solubilize 1.0 cm^3 of 0.1 $mol \cdot dm^{-3}$ $BaCl_2 \cdot 2H_2O$ or $NaCO_3$ aqueous solution into each 33cm^3 of 10vol% $C_{12}E_9$ (or Triton X-100, or Tween-80) solution in cyclohexane (containing 6 vol% *n*-pentanol for Tween-80 system) with vigorous agitation at about 3000 rpm. Mix the same volume of the two microemulsions with the same surfactant, one contains barium ions and the other does carbonate ions, and stir the mixed solution at room temperature slightly. Lay aside for about 12h, and $BaCO_3$ nanowires or nanorods will form.

The samples for TEM (transmission electron microscope; Hitachi, H-800, Japan) observation were prepared by dropping 1~2 drops of the microemulsion solutions containing the $BaCO_3$ products onto a copper grid placed on filter paper and drying in air.

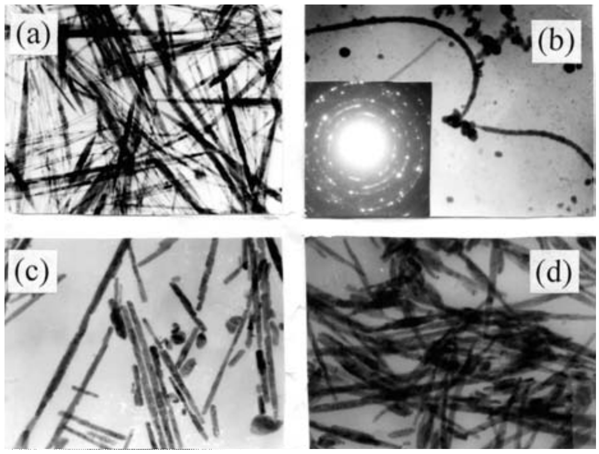

Figure 1. The TEM micrograph (500nm/cm) of one-dimensional nano-structured $BaCO_3$. (a),(b): $C_{12}E_9$ system; (c): Triton X-100 system; (d):Tween-80 system. The inset in (b) indicates the electron diffraction pattern of $BaCO_3$ nanowire.

The direct TEM observation (Figure 1) of the products of the above three systems shows that $BaCO_3$ nanowires (diameters in the range of 10–60 nm and lengths up to some hundreds of micron) and $BaCO_3$ nanorods(diameters and lengths in the range of 30–70 nm and 0.2–3 μm, respectively) can be formed in $C_{12}E_9$ system for the former and in Triton X-100 and Tween-80 systems for the latter. The nanowires can not only be straight (Figure 1a), but also be curved (Figure 1b), which will provide a favorable condition for the industrial application. The nanorods are not rather smooth, but are very straight in Triton X-100 system (Figure 1c) and pointed at ends in Tween-80 system (Figure 1d). The corresponding electron diffraction pattern (inset of Figure 1b) reveals that the $BaCO_3$ nanowires are polycrystals. Figure 2 shows the powder XRD (X-ray diffractometer, Bruker D8 Advance, Germany) pattern of $BaCO_3$ nanowires. All the peaks in the figure can be indexed to be a pure orthorhombic witherite phase $BaCO_3$ with cell constants of a = 0.531nm, b = 0.890nm and c = 0.643nm, which are close to the literature value of Powder Diffraction File.

The composition of the products obtained by the procedure

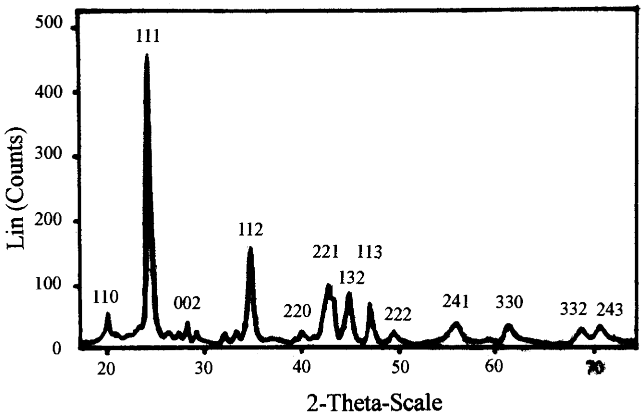

Figure 2. The XRD pattern of $BaCO_3$ nanowires

of demulsification, filtration, washing, desiccation and so on was analyzed by gravimetry for Ba^{2+} and titrimetry for CO_3^{2-}. The results showed that the ratios of Ba^{2+} to CO_3^{2-} in the one-dimensional nanostructured $BaCO_3$ materials were 0.996, 0.991 and 0.994 with respect to $C_{12}E_9$, Triton X-100, and Tween-80 systems respectively, which indicated that both nanowires and nanorods of $BaCO_3$ were pure.

The changes of the experimental conditions can affect the results of the synthesis. If the concentration of Ba^{2+} and CO_3^{2-} is too low, the products will only be $BaCO_3$ particles; conversely, the bulk $BaCO_3$ will form. The volume ratio (ω) of water to surfactant decides the diameters of the aqueous cores(< 10nm for reverse micelles; 10–200nm for microemulsions), and also relates to the diameters of nanowires or nanorods but is not in direct proportion. The volume ratio (ρ) of surfactant to cyclohexane mainly concerns the $BaCO_3$ formation rate. The test results indicated that the favorable ranges of c(Ba^{2+}), c(CO_3^{2-}), γ (= $[Ba^{2+}]/[CO_3^{2-}]$), ω and ρ were 0.05–0.4mol·dm^{-3}, 0.05–0.5 mol·dm^{-3}, 0.6–1.8, 0.2–0.67 and 0.04–0.2, and therefore 0.1mol·dm^{-3}, 0.1mol·dm^{-3}, 1.0, 0.33 and 0.1 were selected, respectively.

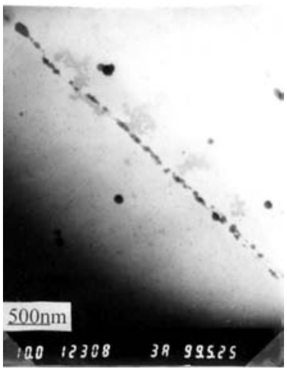

Figure 3. The TEM micrograph of the intermediate captured in the formation course(aged for 8h) of $BaCO_3$ nanowires in $C_{12}E_9$ system.

It can be seen from the above results that the length and the shape of the nanowires or the nanorods are related to the structure of the surfactants, but the crystalline diameters and structure are not. The longer and the more straight the surfactant is, the longer and the more even the nanowires or nanorods are. Perhaps, because there are many branches or one phenyl ring in Triton X-100 and Tween-80, the nanorods in above two systems can not grow long.

Seen from Figure 1, there were some nanoparticles along the nanowires and some fillisters on the nanorods. Figure 3 shows the intermediate separated in the formation course of $BaCO_3$ nanowires, which indicates a directional arrangement of colloidal particles. So, it can be conjectured that the formation of the one-dimensional nanostructured $BaCO_3$ materials in w/o microemulsions belongs to the directional aggregation mechanism of $BaCO_3$ colloid particles controlled by the microemulsion soft templates. The process is probably as follows: first, the formation of $BaCO_3$ colloid particles after mixing the microemulsions containing reactants; next, the directional aggregation of $BaCO_3$ colloid particles; finally, orientated growth of the colloidal particles.

References and Notes

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