Transformation of layered hydroxide zinc benzoate nanosheets into ZnO nanocrystals by electron beam irradiation

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A novel process for synthesis of ZnO nanocrystals from exfoliated layered hydroxide zinc benzoate nanosheets has been developed. In this process, first a layered hydroxide zinc benzoate compound was exfoliated into the layered hydroxide zinc benzoate nanosheets of elementary host layer of the layered compounds in ethanol solvent. This organic-inorganic hybrid nanosheet was transformed into ZnO nanocrystals under electron beam irradiation conditions. The exfoliation reaction of the layered compounds and the transformation reaction from the exfoliated nanosheet into ZnO nanocrystals were investigated using XRD, SEM and TEM analyses. In the structural transformation reaction from the nanosheet into the ZnO nanocrystals, first the benzoate ions on the nanosheet are degraded by electron beam, then the zinc hydroxide become unstable, and finally the nanosheet is dehydrated to ZnO nanocrystals. The ZnO nanocrystals prepared by this process have a crystal size of about 5 nm and high crystallinity.

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1. Introduction

Exfoliation techniques for layered compounds are interesting and useful for the preparation of nanostructured materials.⁽¹⁾ Nanosheets of elementary host layer of the layered compounds with uniform thickness can be obtained by using the exfoliation process, which offers two-dimensional functional nanomaterials. Up to now most studies of the exfoliation reactions have been carried out on the cationic exchangeable metal oxides.^(2,3) The exfoliation techniques for the cationic exchangeable layered compounds can be extensively used in the fabrication of the nanosheets into other nanostructured materials, such as multi-layer thin films by layer-by-layer stacking of different nanosheets,⁽⁴⁾ nanotubes by curling nanosheets,⁽⁵⁾ and nanofibers by splitting nanosheets.⁽⁶⁾ Only a few of studies, however, have been reported on the exfoliation of anionic exchangeable layered hydroxides, and the studies have been limited in layered double hydroxides (LDHs) which can be represented by a general formula of $[M^{II}_{(1-x)}M^{III}_x(OH)_2][X^{n-}_{x/n} \cdot mH_2O]$.⁽⁷⁻¹¹⁾ Very recently, we have succeeded for the first time in the exfoliation of layered hydroxide zinc benzoate compounds⁽¹²⁾ which belong to layered basic metal salts (LBMSs) and can be represented by a general formula of $M^{II}(OH)_{(2-x)}X^{n-}_{x/n} \cdot mH_2O$.^(13,14) This success has provided a new type of organic-inorganic hybrid nanosheets.

ZnO nanomaterials have attracted much attention because of its unique catalytic, electronic, and optical properties as well as its low cost.^(15,16) We think that the layered hydroxide zinc benzoates nanosheets will be a promising precursor in the preparation of the ZnO nanomaterials, because zinc hydroxide can be changed easily to ZnO. In the present study, we describe a novel

process for the preparation of ZnO nanocrystals from the exfoliated nanosheets of the layered hydroxide zinc benzoate compound, which give a new approach for the fabrication of nano-structured ZnO materials.

2. Experimental procedure

A zinc oxide hydrate was prepared by adding a 0.048 M NaOH solution (250 mL) into a 0.024 M $Zn(NO_3)_2$ solution (250 mL) at 4°C. The zinc oxide hydrate (wet sample) containing 6.0 mmol of Zn, desired amount of C_6H_5COOH , and 30 mL distilled water were sealed into a Teflon-lined autoclave with an internal volume of 80 mL, and then was hydrothermally treated at 130°C for 12 h to prepare the layered hydroxide zinc benzoate compounds. A de-benzoated sample of the layered hydroxide zinc benzoate compound was prepared by treating the as-prepared sample of the layered hydroxide zinc benzoate compound (0.3 g) in a mixed solution of water and ethanol (75 mL) containing 10 V% water at a desired temperature for 12 h. The de-benzoated sample (0.1 g) was added into ethanol solvent (25 mL), and then was ultrasonicated for 30 min to exfoliate the layered compound.

Powder X-ray diffraction (XRD) patterns of the samples were carried out on a SHIMADZU XRD-6100 X-ray diffractometer with $Cu K\alpha$ ($\lambda = 0.15418$ nm) radiation. Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-5500S. Transmission electron microscope (TEM) observation and selected-area electron diffraction (SAED) were performed on a JEOL JEM-3010 at 300 kV, and the sample was supported on a microgrid. The exfoliated nanosheet sample supported on the microgrid was irradiated with the electron beam of SAED in the TEM apparatus to prepare ZnO nanocrystals. After the electron beam irradiation, the crystal morphology and structure of the sample were investigated *in situ* in the TEM apparatus.

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3. Results and discussion

Two kinds of the layered basic metal salts were obtained by the hydrothermal treatment of the zinc oxide hydrate and benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$). **Figure 1(a)** and (c) show XRD patterns of samples A and B which were prepared at $\text{C}_6\text{H}_5\text{COOH}/\text{Zn}$ molar ratios of 0.5 and 1.2, respectively, at 130°C . The sample A is a layered phase with a basal spacing of 1.9 nm (1.9 nm layered phase) that shows main diffraction peaks with d -values of 1.898, 0.9529, 0.6365, 0.4756 and 0.2703 nm. The sample B is a mixed layered phase (1.45 nm layered phase) with two basal spacings of 1.45 and 1.31 nm that shows main diffraction peaks with d -values of 1.447, 1.3056, 0.7247, 0.4896, 0.3599, 0.2890 and 0.2464 nm.^{12)–14)} In the previous study, we have prepared the layered hydroxide zinc benzoate compounds using a dried zinc oxide sample as the precursor.¹²⁾ In that case, the single 1.9 nm layered phase was not obtained, but only a mixture of 1.9 nm layered phase and ZnO phase was obtained. In the present study, however, the single 1.9 nm layered phase without ZnO impurity was obtained by using the wet sample of zinc oxide hydrate as the precursor. This result reveals that the wet precursor shows a higher reactivity than the dried one in the formation reaction of the layered compounds.

When the as-prepared samples A and B were treated in the ethanol solution, the exfoliation amounts were very low. To increase the exfoliation amount, the as-prepared samples A and B were de-benzoated by treating the as-prepared samples in the water-ethanol mixed solution at 40 and 60°C , and de-benzoated samples C and D were obtained after the de-benzoate-treatment, respectively. The sample A almost did not change its XRD pattern before and after the de-benzoate-treatment (Figs. 1(a) and (b)). For the sample B, however, XRD pattern changed from 1.45 nm layered phase to 1.9 nm layered phase after the de-benzoate-treatment (Figs. 1(c) and (d)). A TG-DTA analysis indicated that the $\text{C}_6\text{H}_5\text{COO}^-/\text{Zn}$ molar ratio in sample A decreased slightly

from 0.43 to 0.40, while the molar ratio in sample B decreased largely from 1.14 to 0.52 after the de-benzoate-treatments.

SEM observation indicated that the sample A has plate-like particle morphology, and keeps its particle morphology after the de-benzoate-treatment (Figs. 2(a) and 2(b)). On the other hand, the sample B has fibrous particle morphology and the morphology changes to plate-like after the de-benzoate-treatment (Figs. 2(c) and 2(d)). The above results suggest that the 1.45 nm layered phase can be transformed into the 1.9 nm layered phase after the de-benzoate reaction.

Fig. 2. SEM images of (a) sample A (1.9 nm layered phase), (b) sample C obtained by de-benzoate-treatment of sample A at 40°C , (c) sample B (1.45 nm layered phase), and (d) sample D obtained by de-benzoate-treatment of sample B at 60°C .

Fig. 1. XRD patterns of (a) sample A (1.9 nm layered phase), (b) sample C obtained by de-benzoate-treatment of sample A at 40°C , (c) sample B (1.45 nm layered phase), and (d) sample D obtained by de-benzoate-treatment of sample B at 60°C .

■: 1.9 nm layered phase; ●: 1.45 nm layered phase.

Fig. 3. TEM images of layered hydroxide zinc benzoate nanosheets obtained by exfoliation treatments of (a) sample C and (b) sample D in ethanol solvent, and the nanosheets of (c) sample C and (d) sample D after the electron beam irradiation for 30 min at the position without direct irradiation.

The de-benzoated samples C and D can be exfoliated in ethanol solvent, and the saturated concentrations of the exfoliation reaction are 0.38 g/L and 0.66 g/L, respectively. The nanostructure and morphology of the exfoliated samples were investigated by TEM observation. The nanosheet-like particles and curled nanosheet-like particles were observed in the exfoliated samples (Fig. 3), indicating that the de-benzoated samples C and D can be exfoliated into the nanosheets. The formation of curled nanosheet-like particles reveals that the nanosheets are very thin, have high flexibility, and can be curled up during the drying process. The exfoliated nanosheets lose their crystallinities during TEM observation, so that the clear selected-area electron diffraction (SAED) pattern and lattice image for the nanosheets cannot be observed.

In the TEM study, we found an interesting feature that the organic-inorganic hybrid nanosheets can be transformed into ZnO nanocrystals under the electron beam irradiation conditions. Poul et al. have reported also that a layered hydroxide zinc acetate decomposes under electron beam of SAED.¹³⁾ But they did not investigate the decomposition reaction and the formed product. To study the decomposition process and product of the organic-inorganic hybrid nanosheet, we irradiated the nanosheets with electron beam of SAED, and did an *in situ* nanostructural analysis on the structural transformation reaction process using TEM. Before the electron beam irradiation, the nanosheets were uniform (Fig. 4(a)). When the nanosheet sample was irradiated with the electron beam for 5 min, small black maculae on the nanosheets were recognized (Fig. 4(b)). With extending the irradiation time, the maculae become more and more clear. After irradiating for 30 min, the nanosheet changed to ZnO nanocrystals completely (Fig. 4(c)). This sample showed a SAED pattern of four diffraction circularities with *d* values of 0.281, 0.243, 0.160 and 0.133 nm which correspond to the *d* values of (100), (101), (110), and (201) of hexagonal ZnO phase (JCPDS No. 36-1451), respectively (Fig. 4(d)), revealing formation of polycrystalline ZnO. The high-resolution TEM images indicate that this sample shows very clear lattice image with a lattice spacing of 0.247 that corresponds (101) lattice plane of the ZnO phase (Figs. 4(e) and (f)). The lattice images reveal that the polycrystalline ZnO prepared by the electron beam irradiation is constructed by connecting closely ZnO nanocrystals together, where without inter-space between the nanocrystals. The ZnO nanocrystals have a crystal size of about 5 nm, and show high crystallinity. After irradiating for 30 min with the electron beam of SAED, we also observed the nanosheets at other position where without direct irradiation by the electron beam of SAED, and found that the morphology of the nanosheets did not change (Fig. 3(c) and (d)).

In the structural transformation reaction from the organic-inorganic hybrid nanosheet to the ZnO nanocrystals, first the benzoate ions ($\text{C}_6\text{H}_5\text{COO}^-$) combining on Zn(II) of the nanosheet are degraded by electron beam, then the zinc hydroxide becomes unstable, and finally the nanosheet is dehydrated to ZnO nanocrystals. In the previous study, we have developed a thin film process using exfoliated layered metal oxide nanosheet precursor, prepared layered titanate thin film, and transformed the layered titanate thin film into TiO_2 and BaTiO_3 thin films.¹⁷⁾ We think that a thin film of layered hydroxide zinc benzoate nanosheet can be prepared also by using this process, and fabrication and patterning of ZnO nanostructures are possible by the electron beam irradiation of the nanosheet thin film, because electron beam has a wavelength of nanometer-order, which can be focused in nanometer-order size.

Fig. 4. TEM images of samples obtained by electron beam irradiation of the nanosheet sample prepared from sample D for (a) 0, (b) 5, and (c) 30 min, respectively. SAED pattern (d) and high resolution TEM images (e, f) of sample obtained by electron beam irradiation for 30 min.

4. Conclusions

The wet sample of zinc oxide hydrate shows high reactivity with benzoic acid in the formation of the layered hydroxide zinc benzoate compounds. The layered compounds can be de-benzoated by treatment in the water-ethanol mixed solution. The de-benzoated layered compounds can be exfoliated easily to the organic-inorganic nanosheets in ethanol solvent. The nanosheet can be transformed into ZnO nanocrystals by electron beam irradiation, which provides a novel process for the preparation of ZnO nanomaterials.

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