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A general method for fabricating nanorods

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Abstract

We introduced a general slow-precipitation method for fabricating nanorods. By this method, Gd(OH)₃ nanorods with a length of 300 nm and a width of 20 nm were fabricated in the middle of still double-layer solutions, composed of the Gd(NO₃)₃ and NaOH solutions. The products present a one-dimensional nanostructure in a very wide range of NaOH concentrations. On increasing the NaOH concentration, the aspect ratio of the Gd(OH)₃ rods changed from 3 to 15. To validate the generality of this method, ZnS, NiS and PbS nanorods were also fabricated by it.

The fabrication and characterization of one-dimensional (1D) nanostructured materials has attracted much interest, owing to both their novel physical properties, which differ from those of bulk materials, and their potential applications in nanodevices [1–7]. For the fabrication of nanorods, the first method was that Ag nanorods were synthesized by using selective surfactant [8]. Then InAs nanorods were prepared by utilizing metal catalyst particles [9], and CdSe nanorods were fabricated by controlling the growth kinetics [10]. To fabricate nanorods of new materials, it is often difficult to utilize the above methods due to the too rigorous reaction conditions or the proper surfactants, catalyst particles and ligands are usually one in a thousand. In this paper, we introduce a general slow-precipitation method for fabricating nanorods. By this method, Gd(OH)₃ nanorods were first fabricated due to it is the precursor of Gd₂O₃:Eu, which is a good luminescent material.

In the experiments, Gd(NO₃)₃ solution was prepared by mixing 0.3625 g Gd₂O₃ (99.999%) with 50 ml distilled water and adding appropriate HNO₃ to the mixture with proper stirring to form a clear solution. This solution was diluted to 100 ml by adding more distilled water. Then, 10 ml Gd(NO₃)₃ solution (0.02 M), 1 ml distilled water and 10 ml NaOH solution (of 0.06, 0.12, 0.18, 0.24, 0.30, 0.36, 0.42, 0.48, and 0.54 M, respectively) were extracted in the injectors, respectively. The precipitates, which can be suspended in water for several days, formed in the middle of the solution

pole within 1 min. Third, the injectors stayed on a rack for four days. This long time is necessary for the reaction to be complete, because the ion diffusion is very slow when the solution is still. Finally, the white precipitates in the injector were separated by centrifugation, and washed with distilled water. These centrifugation and washing procedures were repeated twice. All the included operations were performed at room temperature. A schematic drawing of the above experiments is shown in figure 1. The precipitates after four days were taken as the final products.

These products were observed in a transmission electron microscope (TEM). Figure 2(a) shows a high magnification TEM image of the sample (from 0.24 M NaOH solution). It is mainly composed of Gd(OH)₃ nanorods 300 nm long and 20 nm wide. That is to say, the aspect ratio of these rods is about 15. To affirm that the nanorods were Gd(OH)₃ crystals, we took an electron diffraction pattern of the sample. As shown in figure 2(b), it shows a hexagonal structure of Gd(OH)₃ ($a = 6.329 \text{ \AA}$ $c = 3.631 \text{ \AA}$; PDF#: 832037). The corresponding crystal indices are marked in the diffraction image. So, the fabricated nanorods (from the 0.24 M NaOH solution) are confirmed to be Gd(OH)₃ crystals. Samples from the 0.18 and 0.30 M NaOH solutions had morphologies that were similar to the one from the 0.24 M NaOH solution.

For the samples from 0.06 and 0.12 M NaOH solution, as shown in figure 3(a), the product is mainly composed of 120 nm long and 40 nm wide Gd(OH)₃ nanorods. Their aspect ratio is only about 3.

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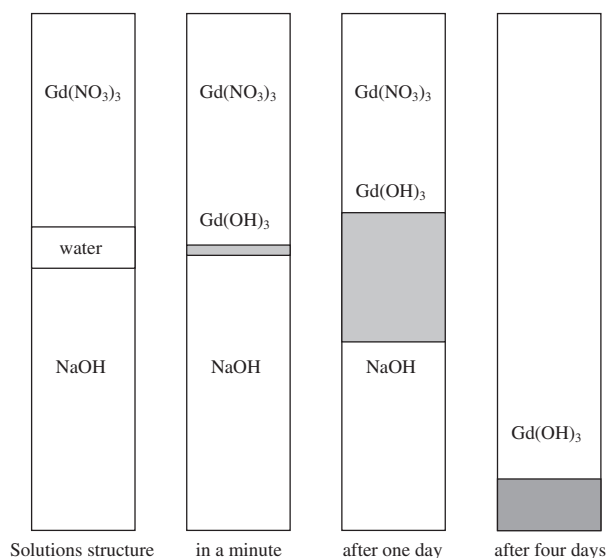


Figure 1. A schematic drawing of the experiments.

With the increase of the NaOH concentration, as shown in figure 3(b), for the samples from the 0.36, 0.42, 0.48, and 0.54 M NaOH solutions, the precipitates are composed of $\text{Gd}(\text{OH})_3$ nanorods with lengths of several microns and widths of several hundreds nanometres. Considering the results of the above experiments, we concluded that, by this slow-precipitation method, $\text{Gd}(\text{OH})_3$ nanorods could be fabricated in a very wide range of the NaOH concentrations.

We believe the formation mechanism of $\text{Gd}(\text{OH})_3$ nanorods is as follows. When $\text{Gd}(\text{NO}_3)_3$ solution was directly mixed with NaOH solution with stirring, the precipitation was often composed of quasi-spherical $\text{Gd}(\text{OH})_3$ nanoparticles of about 50 nm. This reveals that a short growth period and a severe nucleation process took place [11]. In this slow-precipitation experiment, when NaOH solution was extracted into the injector, the light impact between the $\text{Gd}(\text{NO}_3)_3$ and NaOH solutions made the Gd^{3+} and OH^- ions mix sufficiently at the interface between the two solutions. This resulted in a lot of spontaneous $\text{Gd}(\text{OH})_3$ nuclei. With increasing time, the solutions became still. The ions moving to the interface were mainly transported by static diffusion. Because the static diffusion coefficient is roughly one thousandth of the coefficient with stirring, in the interface region, the concentration of ions (Gd^{3+} and OH^-) became very low. On the one hand, this low reactant concentration means there is no second nucleation. On the other hand, the low reactant concentration results in slow reaction. The numbers of created $\text{Gd}(\text{OH})_3$ monomers are not sufficient to grow on all the surfaces of the nuclei with a size large than a critical one. The limited monomers only grew on preferential surfaces which are determined by the nature of $\text{Gd}(\text{OH})_3$ crystal. This formed the anisotropy nuclei. During the crystal growth process, the subsequent $\text{Gd}(\text{OH})_3$ monomers always grew on this preferential surface. And so the nanorods formed.

To verify our proposed formation mechanism, we picked up the $\text{Gd}(\text{OH})_3$ precipitates (from the 0.18 M NaOH solution) after they had stayed on the rack for one, two, and three days. As shown in figures 4(a)–(c), the precipitates (after one day) are $\text{Gd}(\text{OH})_3$ nanoparticles of about 5 nm; after two days they

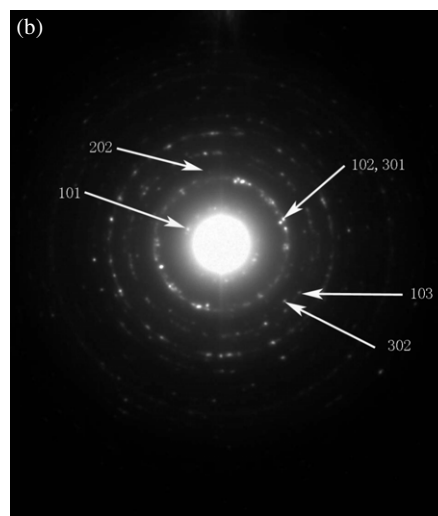
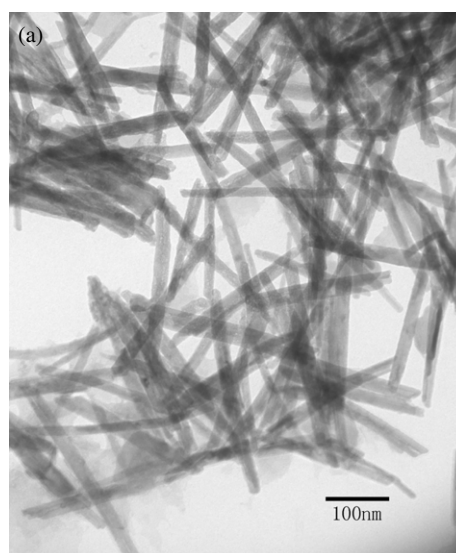


Figure 2. (a) A TEM image of the nanorods from the 0.024 M NaOH solution. (b) The electron diffraction pattern of the nanorods shown in (a).

are $\text{Gd}(\text{OH})_3$ nanoparticles of about 8 nm; the products after three days are $\text{Gd}(\text{OH})_3$ nanorods with a length of 50–100 nm and width of 8–15 nm. From the experimental results, we can know that when the size of the $\text{Gd}(\text{OH})_3$ nanoparticles is lower than 8 nm, the $\text{Gd}(\text{OH})_3$ particles keep a spherical shape and grow with increased time. But when the size of the $\text{Gd}(\text{OH})_3$ nanoparticles is larger than 8 nm, the $\text{Gd}(\text{OH})_3$ particles exhibit rod shapes and grow anisotropically. This result is well consistent with our proposed formation mechanism.

For the effect of the NaOH concentration on the aspect ratio of $\text{Gd}(\text{OH})_3$ rods, the following explanation is provided. Under the condition of low NaOH concentration, the critical size of spontaneous nuclei is large. This leads to the number of spontaneous nuclei being small. The slow diffusion of the ions can supply $\text{Gd}(\text{OH})_3$ monomers for growth with a steady low rate. Because the nanorods formed at the condition of the number of created $\text{Gd}(\text{OH})_3$ monomers are not sufficient to grow on all the surfaces of the nuclei with a size larger than a critical one, when the number of nuclei is small, the steady monomer supply can naturally support the isotropic

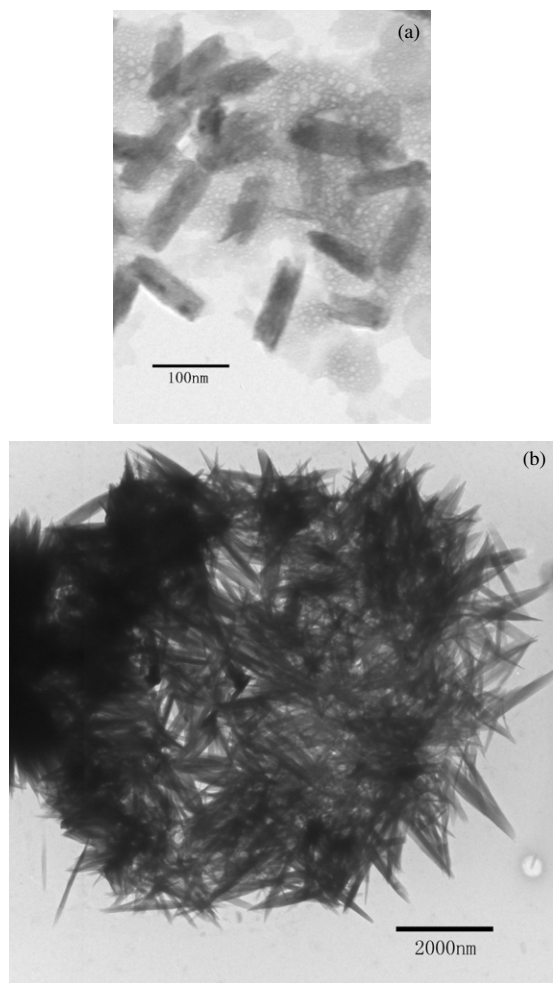


Figure 3. (a) A TEM image of the nanorods from the 0.006 M NaOH solution. (b) A TEM image of the nanorods from the 0.054 M NaOH solution.

nuclei reaching a large size. Under the condition of high NaOH concentration, the critical size of $\text{Gd}(\text{OH})_3$ nuclei is small, and this will result in the number of formed nuclei being large. With a fixed supply of $\text{Gd}(\text{OH})_3$ monomers, the nuclei can only keep their isotropic shape with a smaller size. During the anisotropic growth, the high NaOH concentration formed high aspect ratio rods with the diameter of the fabricated nanorods being determined by the size of the anisotropic nuclei.

To validate this method's generality for a broad spectrum of materials, ZnS nanorods were fabricated with 0.01 M $\text{Zn}(\text{NO}_3)_2$ and 0.03 M Na_2S solutions; NiS nanorods were fabricated with 0.01 M $\text{Ni}(\text{NO}_3)_2$ and 0.03 M Na_2S solutions; and PbS nanorods were fabricated with 0.005 M $\text{Pb}(\text{NO}_3)_2$ and 0.015 M Na_2S solutions. To make the cations and anions simultaneously diffuse to the interface region, we experimentally chose excessive anion concentration (by a factor of three) to accelerate the diffusion of the large anions. The precipitation of ZnS (white) and NiS (black) is similar to that of $\text{Gd}(\text{OH})_3$, of which the natant precipitates can remain unchanged in the interface (reaction) area for several days. But in the precipitation of PbS (black), the precipitates settle down at the bottom in 1 h. As shown in figures 5(a)–(c),

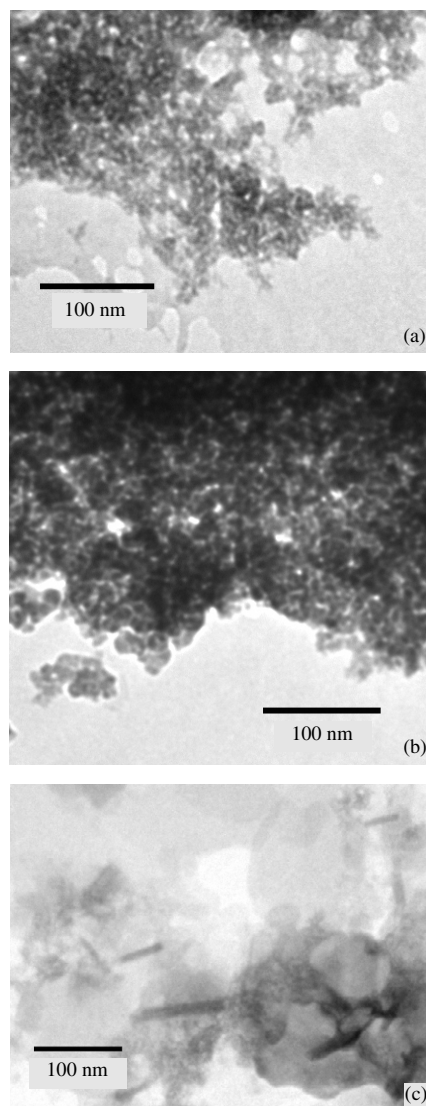


Figure 4. (a) The precipitation after one day (from 0.18 M NaOH solution). (b) The sample after two days (from 0.18 M NaOH solution). (c) The product after three days (from 0.18 M NaOH solution).

the observation of these samples showed that the samples of ZnS, NiS are composed of nanorods with a length of several hundreds nanometres and a width of 20, and 60 nm; however, the PbS sample was composed of nanorods with a length of several tens of nanometres and a width of 20 nm, that is to say the aspect ratio of PbS rods is less than 3. Figure 5(d) is a selection area diffraction (SAD) pattern of PbS nanorods. It shows the cubic structure of PbS ($a = 5.934 \text{ \AA}$; PDF#: 770244). The corresponding crystal indices are marked. So, the fabricated PbS nanorods are confirmed to be crystalline. The fabricated ZnS nanorods were also confirmed to be crystalline from the UV absorption spectrum. As shown in figure 6, the absorption edge is at 343 nm (3.62 eV), which is in agreement with the energy gap of cubic ZnS. So by this method, the fabricated rods are shown to be crystals. For the formation progress of the nanorods, the TEM picture of the PbS sample presented the anisotropic nuclei

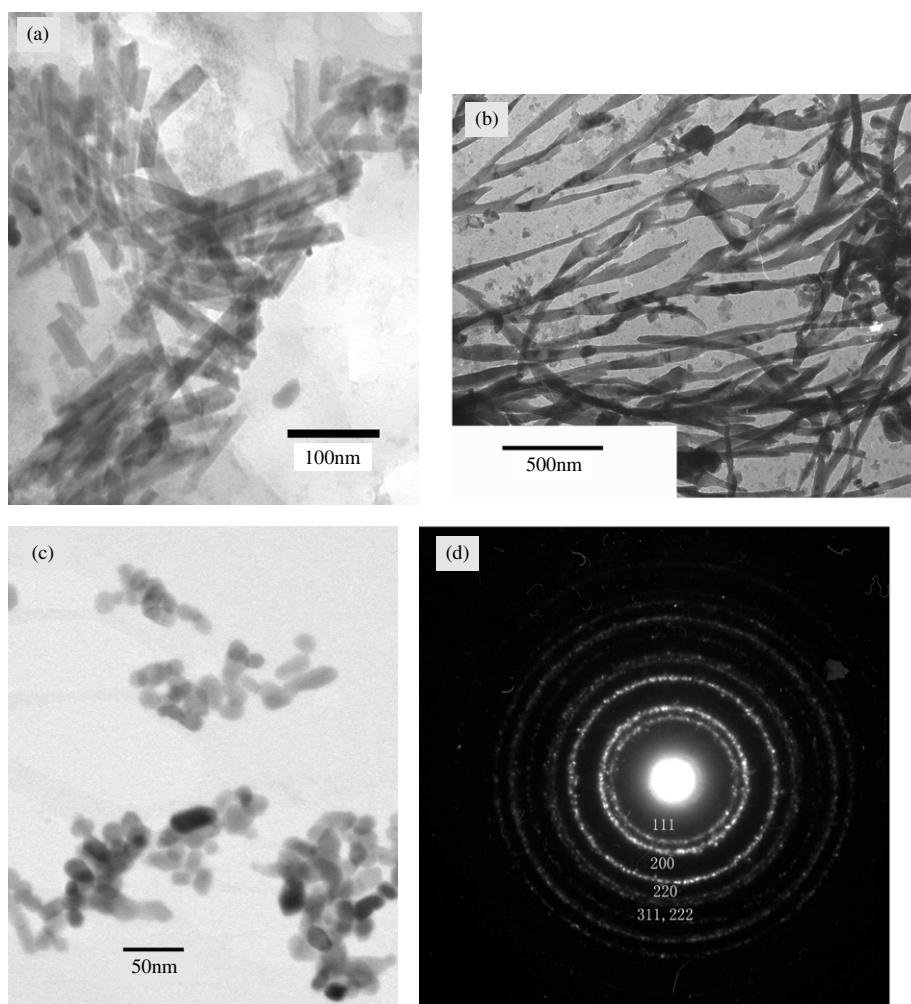


Figure 5. (a) A TEM image of the ZnS nanorods from the 0.001 M $\text{Zn}(\text{NO}_3)_2$ and 0.003 M NaS solutions. (b) A TEM image of the NiS nanorods from the 0.01 M $\text{Ni}(\text{NO}_3)_2$ and 0.03 M Na_2S solutions. (c) A TEM image of the PbS nanorods from the 0.005 M $\text{Pb}(\text{NO}_3)_2$ and 0.015 M Na_2S solutions. (d) An SAD pattern of the PbS nanorods.

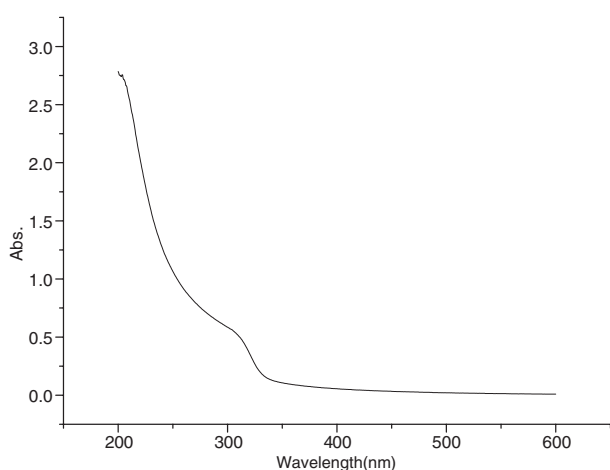


Figure 6. The UV spectrum of the ZnS nanorods.

formed from the isotropic ones. Considering the fast settling of the PbS precipitation, we think that the short PbS rods are due to the PbS nuclei moving out of the reaction region in 1 h.

At this point, the result of short PbS rods also validates the proposed rod formation model.

In conclusion, when the solutions are still, the reaction is localized in the interface region and becomes too slow to form new nuclei. This can effectively reduce the number of nuclei and extend the crystal growth process. During the growth process, $\text{Gd}(\text{OH})_3$ nanorods with a length of 300 nm and a width of 20 nm formed at the interface region of the still $\text{Gd}(\text{NO}_3)_3$ and NaOH solutions. Our experimental results show that one-dimensional nanostructured products can be fabricated in a very wide range of NaOH concentrations. To validate the generality of this method, ZnS, NiS and PbS were also fabricated by it. Because this method is based on the common precipitation system, we can expect other novel nanorods to be fabricated by it.

Acknowledgments

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